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## CONTENTS

H. G. DERX: "The oxidative cleavage of fats by fungi". (Communicated by Prof. G. VAN ITERSON Jr,), p. 96.

ERNST COHEN, WILHELMA A. T. DE MEESTER and A. L. TH. MOESVELD: "The Influence of Pressure on the Solubility of Substances V. The system Naphtalene-Tetrachlorethane", p. 108.

H. J. CHOUFOER: "On Disaccharins". (Second preliminary communication). (Communicated by Prof. A. F. HOLLEMAN), p. 119.

S. GOUDSMIT, J. VAN DER MARK and P. ZEEMAN: "Magnetic Resolution of the Scandium Spectrum". (First part), p. 127.

A. A. NIJLAND: "The Light-Curve of the Cepheids", p. 142.

W. H. JULIUS: "The Evershed effect in the spectrum of sun-spots", p. 150.

F. A. H. SCHREINEMAKERS: "Equilibria in systems, in which phases, separated by a semi-permeable membrane" IV, p. 157, Ibid. V, p. 166.

G. H. DIEKE: "On the Structure of the Ultra-Violet Bands of Water Vapour". (Communicated by Prof. P. EHRENFEST), p. 174.

SHIN-ICHI HIBINO: "Conditions influencing the production of colouring matter of Monascus purpureus WENT". (Communicated by Prof. F. A. F. C. WENT), p. 182.

L. RUTTEN: "On the Direction of the Tertiary Mountain-building Movements in the Island of Java", p. 191.

L. BOLK: "On the existence of a dolichocephalic race of Gorilla", p. 204.

R. WEITZENBÖCK: "Ueber projectieve Differentialinvarianten" III, p. 214.

## **Chemistry.** — "*The oxidative cleavage of fats by fungi*". By H. G. DERX. (Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of June 28th, 1924).

In order to obtain a general insight of the metabolic changes which food undergoes in the living organism, it is necessary to isolate intermediate products which may appear during the decomposition of the food-stuffs. Nevertheless the solution of this problem is not easy, for in the normal healthy organism these intermediate products are often of such transient character that their existence cannot be indicated. In a few cases, however, they have been successfully isolated by the use of various special devices, of which further mention will be made.

The study of the decomposition products of carbohydrates has received most labour and care at the hands of physiologists, and one of the most important recent results to which KLUYVER [1]) has called attention, is the demonstration that in the course of metabolic processes in microorganisms a unity is found that at first sight seems incredible.

For a general review of the various microbiological processes the reader is referred to this highly interesting paper, in which this unity is clearly demonstrated, and I venture to borrow one example from this essay in order to elucidate this point.

It is well known that the investigations of NEUBERG have shown that acetaldehyde is an important intermediary product in the formation of alcohol from sugar by saccharomycetes, but this substance (acetaldehyde) has also been demonstrated during the fermentation of carbohydrates by coli-bacteria (formation of lactic acid, acetic acid, succinic acid, etc.), by butyric acid bacteria (formation of butyric acid, acetic acid, etc.) and by cellulose-decomposing bacteria (formation i.a. of butyric acid, acetic acid, etc.). It has been found that acetaldehyde is also produced in the oxidative cleavage of sugars by the most divergent species of fungi from the group of Mycomycetes (Monilia candida, Oospora lactis, Aspergillus cellulosae B) as well as from the group of Phycomycetes (Mucor racemosus, Mucor rouxii) [2]).

A second example is furnished by the investigations of M. MOLLIARD with Aspergillus niger [3]). MOLLIARD demonstrated that, in the oxidation of sugar, it is possible, by regulating the nitrogen or phosphorus in the substrate, to produce either gluconic acid, citric acid or oxalic acid (and — or — carbonic acid) as the chief product. These are substances which, up to the present, have been considered as „specialities" from vinegar bacteria, Citromyces species, Aspergillus niger and — other fungi. Thus oxalic acid may be formed in considerable quantities, not only by Aspergillus niger, but also, under certain circumstances, by different vinegar bacteria [1]).

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[1]) A. J. KLUYVER, Eenheid en Verscheidenheid in de stofwisseling der microben. Chem. Weekbl. **21**, 266—277 (1924).

[2]) CLARA COHEN, Bioch. Zeitschr. **112**, 139—143 (1920).

[3]) M. MOLLIARD, Compt. rend. biol. **72**, 479 (1920), ibid. **87**, 967 (1922).
„ „ C.R. **174**, 881 (1920), ibid. **178**, 161 (1924).

These and many other facts point to a gradual cleavage — and in an analogous way — of carbohydrates by widely different microorganisms.

But at the same time it is well known that the conclusions of microbiologists also enter into the domain of animal and vegetable physiology. Very justly animal physiologists suppose that the source of lactic acid in the muscular tissue is to be found in the carbohydrates. Further, G. M. MEYER [2]) found that leucocytes oxidize hexoses (not pentoses) to lactic acid. EMBDEN and his co-workers [3]) found formation of lactic acid in liver rich in glycogen, expressed muscle juice etc. The presence of oxalic acid in urine, in species of Oxalis and of Rheum, of citric acid in milk and in unripe lemons not only points to the fact that these substances are of general occurrence in nature, but also shows that in all living beings they originate in an analogous way. And there is much truth in the words of MAX RÜBNER, when he says: "Was lebt ist Eins, daher muss trotz der Varianten, welche die einzelnen Spezies vorstellen, in ihrem Leben das gemeinsame Bild des Ganzen sich widerspiegeln." [4])

As has already been observed, it is not always easy to detect and to isolate the intermediate products of metabolic processes; generally the oxidation of the food is so intensive that intermediate products are out of the question. This is obvious, for the energy necessary to the organism's growth, reproduction, mechanical labour, etc. is eventually produced by a chemical process, viz. — the combustion of the foodstuffs. The amount of energy set free by this process increases according to the completeness of the oxidation. Incomplete combustion, or in other words, cessation of oxidation by formation of intermediate products, may in a certain sense be considered as a divergence, often brought about by unfavourable physiological conditions, e.g. by lack of oxygen, of assimilable nitrogen etc., in general by unsuitable quantitative or qualitative composition of the food, by temperature sensibly different from that of optimum growth, by the accidental presence of narcotics etc.

Naturally, this does not preclude the existence of special species having permanently weak oxidative capacity even under the most favourable conditions; on the contrary, it points to the possibility that such hereditarily constant forms originate from adaptation to definite nutritional conditions. Compare e.g. Acetobacter xylinum, BROWN and Acetobacter suboxydans, KLUYVER and DE LEEUW [1]).

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[1]) ZOPF, Ber. d. deutsch. Bot. Ges. **18,** 32, BANNING, Z. f. Bakt. II Abt., **8,** 395 (1902).

[2]) G. M. MEYER, Journ. of biol. Chem. **11,** 353—361 (1912).

[3]) EMBDEN, Bioch. Zeitschr. **45,** (1912). Vide also O. HAMMARSTEN, Lehrbuch der physiologischen Chemie, 9th edition, Munich. 1922.

[4]) MAX RÜBNER, Ernährungsphysiologie der Hefezelle bei alcoholischer Gärung. Leipsic, 1913, page 1.

But, on the other hand, it is certain that Saccharomycetes thrive only when a sufficient supply of oxygen is at their disposal:

Under these circumstances an important part is played by the oxidative cleavage of sugar to carbonic acid and water, and on account of the vigorous growth of the yeast an apparently increased production of alcohol is observed. In a similar way an accumulation of oxalic acid in cultures of Aspergillus niger is possible only when there is a lack of assimilable nitrogen, or when growth takes place at lower temperatures. Under favourable circumstances there is very little formation of oxalic acid. [2])

In consequence, I am of opinion that a wider meaning may be taken from the words of DUCLAUX regarding the formation of oxalic acid:,, C'est un produit de souffrance". This will appear more clearly in the subsequent course of my paper.

So far, views on the oxidation of fats in the living organism have been expressed rather by zoological physiologists than by microbiologists, though this is not the case with the oxidation of carbohydrates. This is clearly shown by the work of PIERRE WORINGER [3]) and by the voluminous list of the literature he mentions. As the oxidation processes in the higher animals and in microorganisms are analogous it may be interesting to trace the methods applied by physiologists in these researches. We find here five fundamentally different methods of procedure:

1. The indirect method, consisting of the investigation of the oxidative capacity of the organism in respect to intermediate products theoretically possible.
2. The introduction into the molecule of a group difficult to oxidize, e.g. the benzene nucleus, in order to prevent complete combustion.
3. The perfusion of isolated surviving organs.
4. Administration of the substance under investigation to individuals having definite pathological disturbances of the dissimilation processes, e.g. diabetics (induced or otherwise), alcaptonurics, etc.
5. Subcutaneous or intravenal injections of large quantities of the substance to be investigated.

The methods given under headings 1. and 2. and sometimes 3. (expressed juices) can be applied to microorganisms.

One of the fundamental results of the above mentioned investigations is the discovery that the oxidation of normal fatty acids commences at the $\beta$-carbon atom with formation of a ketonic acid. The latter splits off acetic acid, so that a fatty acid with two C atoms less than the original fatty acid results, and so on [1]. The $\beta$-ketonic acid may under certain circumstances be reduced to a $\beta$-hydroxy acid, the action being reversible. On the other hand $CO_2$ may be split off with the formation of methyl-ketone, but this must be considered an abnormal decomposition product.

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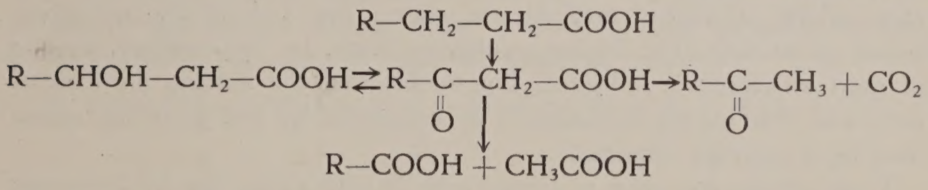
[1]) A. J. KLUYVER en DE LEEUW, Tijdschr. v. Verg. Geneesk., **10**, Afl. 2—3 (1924).

[2]) EMMERLING, Z. f. Bakt. II Abt., **10**, 274 (1903).

[3]) P. WORINGER, La dégradation des acides gras dans l'organisme animal, Paris, MASSON & Cie.

The following scheme demonstrates the reactions under discussion:



$$\begin{array}{c} R{-}CH_2{-}CH_2{-}COOH \\ \downarrow \\ R{-}CHOH{-}CH_2{-}COOH \rightleftarrows R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_2{-}COOH \rightarrow R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}CH_3 + CO_2 \\ \downarrow \\ R{-}COOH + CH_3COOH \end{array}$$

## *Experimental.*

If we introduce mould spores into a RAULIN-DIERCKX solution [2] which contains ammonium nitrate and ammonium phosphate as source of nitrogen,

TABLE I.

Fungus: Penicillium cyclopium [3]; Nutrient medium: Raulin-Dierckx solution.
T = 22°–25° C.

| Substance added | Butyric acid | Valeric acid | Caproic acid | Caprylic acid | Capric acid | Lauric acid | Myristic acid | Palmitic acid | Stearic acid | Oleic acid | Elaïdic acid | Brassidic acid | Control |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As fatty acid | — | — | — | — | (∓) K | ± K | + | ++ | ++ | + | ++ | ++ | + |
| As K-salt | + | + | ± K | ∓ K | (∓) K | (∓) K | ∓ K | ± | + | + | + | + | + |

Signs: — no growth; (∓) very feeble growth after 2 weeks;
∓ very feeble growth; ± feeble growth; + vigorous growth;
++ very vigorous growth; K formation of Ketones.

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[1] Compare F. KNOOP, Beitr. z. chem. Phys. u. Path. **6**, 150 (1905), **11**, 411 (1908).

[2] Vide PH. BIOURGE, Les moisissures du groupe Penicillium Link, La Cellule **33**, 43 (1923). The preparation is as follows:

1. Dissoudre 0,40 de carbonate de magnésie dans une fiole jaugée de 100 $c^3$ au moyen de 0,71 d'acide tartrique.
2. Dans un ballon jaugé d'un litre, contenant 800 à 900 gr. d'eau distillée, dissoudre: saccharose 46,6; nitrate d'ammoniaque 2,66; phosphate d'ammoniaque 0,40; carbonate de potassium 0,40; sulfate d'ammonium 0,16; sulfate de zinc 0,04; sulfate ferreux 0,04.
3. Ajouter 66—67 $c^3$ de la solution de tartrate magnésique et compléter jusqu'au trait de jauge.

[3] A very common kind of the long series of blue-green Penicilliums, which are always erroneously indicated by the generic name of "Penicillium glaucum".

and saccharose as source of carbon, and add $^1/_4$ % of fatty acid in the one case and $^1/_4$ % of the corresponding potassium salt in the other, we are able, after leaving the cultures for four days at 22—25° C. to demonstrate the results drawn up in table I (page 99).

This table shows at a glance that the lower fatty acids, up to and including lauric acid, hinder the growth very markedly. It must, however, be taken into consideration that the acids from caprylic upwards do not completely dissolve under the experimental conditions, but even lauric acid, which is almost insoluble in water, has a decidedly preventive action on growth. The higher solid fatty acids, on the contrary, appear to exert a favourable influence. But in this case the floating particles of fatty acid tend to act mechanically as a support for the mycelium rather than as a nutritive substance.

These results are quite in accord with TRAUBE's rule, but are somewhat obscured by the unfavourable influence caused by the increase of the H-ion concentration of the lower acids (brought about by their greater solubility). In the investigations with potassium salts, where the $P_H$ at the commencement of the experiment was always regulated to 6 to 7, the latter influence did not appear and TRAUBE's rule held good in every respect[1]). The fatty acids formed by hydrolysis of their salts are adsorbed on the mycelium:

In the case of potassium caproate enough free undissociated caproic acid is present in the liquid to markedly hinder oxygen resorption by the adsorption of the acid on the young submersed mycelium. This is also the case with the caprylate, caprate, laurate and myristate of potassium, whereas, with the salts of the higher acids, notwithstanding their hydrolysis, the concentration of free fatty acid in the aqueous solution is too small to appreciably obstruct oxygen assimilation. The normal growth in the case of the higher soaps shows at the same time that only the fatty acid molecules in the solution have a narcotic action, and not the soapmicels or other complexes. The assimilation of oxygen is thus impeded (and this is in agreement with the ideas of WARBURG[2]) regarding surface catalysis) by this adsorption of fatty acids on the young submersed mycelium and, consequently, oxidation of food-stuffs (sugar and fatty acid) is strongly checked. And in fact Table I shows that ketones are formed in every case where growth is impeded, but not completely prevented. These ketones may be isolated by distillation, followed by neutralisation and extraction with ether, and may be identified as semicarbazones. This showed that each fatty acid gave rise to one specific ketone, thus:

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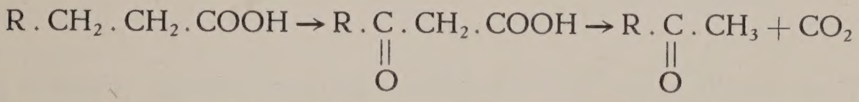
[1]) Oleic acid, Elaïdic acid, and Brassidic acid do not belong to this homological series. This is perhaps the cause of the anomalous behaviour of oleic acid and its potassium salt.

[2]) Compare H. FREUNDLICH, Kapillarchemie, 2, Auflage. Leipsic 1922.

| | | |
|---|---|---|
| caproic acid | yielded | methyl-propylketone |
| caprylic acid | „ | methyl-amylketone |
| capric acid | „ | methyl-heptylketone |
| lauric acid | „ | methyl-nonylketone. |

In the case of myristic acid the quantity of ketone formed was too small for analysis, but we may doubtless assume that myristic acid will give rise to methyl-undecylketone.

The result is thus unequivocal. In no other way can we demonstrate so clearly that oxygen attacks at the $\beta$-position in the molecule. As was to be expected, the reaction takes the following course:



$$R\,.\,CH_2\,.\,CH_2\,.\,COOH \rightarrow R\,.\,\underset{\underset{O}{\|}}{C}\,.\,CH_2\,.\,COOH \rightarrow R\,.\,\underset{\underset{O}{\|}}{C}\,.\,CH_3 + CO_2$$

But once more I wish to emphasize the fact that this formation of ketones manifests itself only when growth is impeded, and that ketones are not normal intermediate products in the biological oxidation of fatty acids: „Ce sont des produits de souffrance.'' [1])

If we attempt to isolate the volatile ketones in duplicate cultures about ten days old, we find that they have disappeared. This disappearance is found to occur pretty well at the time when the mycelium raises itself in the air, begins to form conidiophores and puts forth the green conidia.

Evidently respiration is no longer impeded, growth becomes normal, and the ketones (which also have a narcotic action) are further broken up.

The formation of ketones is not restricted to free fatty acids and their soaps; fats themselves may lead to the formation of ketones. It follows, however, from the preceding work that the formation of ketones is to be expected only in such fats as contain the lower fatty acids. The best known of these fats are coconut oil (Cocos nucifera), palm-kernel oil (Elaeis guineensis), babassu oil (Attalea funifera), cohune oil (Attalea cohune), and a few other fats obtained from seeds of various species of palm, and finally butterfat.

For the purposes of this paper we shall restrict ourselves to coconut oil and butterfat.

Older investigations show that it is extremely probable that the primary action of a fungus on neutral fat is a splitting into fatty acid and glycerine by a mould lipase. Such lipase is usually present in the substrate of Penicillium cultures and can readily be demonstrated by well-known processes. Further, it is certain that glycerine can serve as a source of carbon for most fungi, but the fatty acids will, or will not, have a narcotic action, according to the conditions and to their places in the homologous series. The following experiments may serve as an illustration.

Three species of Penicillium, all generally designated as „Penicillium glaucum" were tested using the saccharose containing RAULIN-DIERCKX solution to which 1 % of coconut oil had been added.

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[1]) DUCLAUX, loc. cit.

TABLE II [1]).

| | Raulin Dierckx + 1 % coconut oil | Control without coconut oil |
|---|---|---|
| Penicillium cyclopium Westling. | + | + |
| „ leucopus Biourge. | ± K | + |
| „ Roquefort Thom. | + | + |

These results show that Penicillium leucopus, Biourge produces so much fatty acid — evidently on account of a very vigorous lipase activity — that its growth is suppressed. Only in this instance is ketone produced, no trace whatever of ketone being formed with the other Penicillia.[2]) Should the medium contain only inorganic salts and coconut oil with no saccharose [3]) the results are entirely different.

TABLE III [1]).

| | Inorganic nutrient medium + 1 % coconut oil | |
|---|---|---|
| | After 4 days | After 14 days |
| Penicillium cyclopium Westling. | ± K | ++ |
| „ leucopus Biourge. | ± K | ++ |
| „ Roquefort Thom. | ± K | ++ |

In these experiments all three species formed ketones. In this medium glycerine is the source of carbon, being formed together with about seven times its weight of fatty acids by the action of the mould lipase. Under these unfavourable circumstances it is evident that ketones must be formed. But at the same time the experiments show that here also after the lapse of two weeks ketones had entirely disappeared.

If these experiments are now repeated using butterfat instead of coconut oil in the same inorganic medium no trace of ketone can be detected, even under these unfavourable biological conditions. This, at first sight unexpected, result is to be explained by the difference in composition of coconut oil and butterfat.

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[1]) For explanation of the signs see Table I.

[2]) This shows how the use of the collective name of "Penicillium glaucum" may give rise to contradictory data in the literature. Such contradictions are indeed very frequent.

[3]) This nutrient medium, which was also used for the other experiments mentioned, contains: Water 1000; Ammoniumnitrate 2,5; Ammoniumphosphate 0,5; Monopotassium-phosphate 0,5; Magnesiumsulphate 0,5; Zincsulfate 0,04; Ferrosulfate 0,04; parts by weight.

TABLE IV.

| | Fatty acids from coconut oil 1) | | Fatty acids from butter 2) | |
|---|---|---|---|---|
| Butyric acid | — | 66 % | ± 3.6 % | ± 13.6 % |
| Caproïc acid | 2 % | | ± 1.9 % | |
| Caprylic acid | 9 % | | ± 0.7 % | |
| Capric acid | 10 % | | ± 1.4 % | |
| Lauric acid | 45 % | | ± 6.0 % | |
| Myristic acid | 20 % | | ± 18.7 % | |
| Palmitic acid | 7 % | | ± 29.5 % | |
| Stearic acid | 5 % | | ± 5.4 % | |
| Oleic acid | 2 % | | ± 32.8 % | |
| Dioxy-oleic acid | — | | | |

Coconut oil thus contains about 5 times the quantity of volatile, ketone-forming fatty acids contained in butterfat. It need hardly be pointed out that this is of great importance when we take into consideration the fact that the fatty acids, liberated by lipase, partly remain in solution in the fat. Yet it can scarcely be doubted that under still more unfavourable conditions, e.g. by culture in an atmosphere deficient in oxygen, or by symbiotic culture with a vigorous fat-splitting organism, ketones may also appear in butterfat.

The ketones formed from fatty acids all have a very characteristic odour, which is particularly intensive in the cases of methyl-propyl-, methyl-amyl- and methyl-heptyl-ketones so that in investigations with the odourless coconut oil the appearance of this odour may be considered a very sensitive reaction for ketone-formation. These strongly odoriferous substances have from time to time attracted the attention of investigators and the following is a short summary of our present knowledge regarding them.

Haller and Lassieur 3) found in the unsaponifiable part of coconut

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1) Elsdon, Analyst, **38,** 8 (1913).

2) Means of analyses published by Koefed, Analyst, **17,** 130 (1892). Browne, Journ. Am. Chem. Soc. **21,** 807, (1899), and Holland and Buckley, Journ. Agric. Research **12,** 719 (1918).

3) Haller and Lassieur, Compt. rend. **150,** 1013 (1910), **151,** 697 (1910).

oil traces of an unknown aldehyde, methyl-n-nonyl ketone (75 %), methyl-n-heptyl ketone, methyl-n-undecyl ketone (small quantity) and methyl-n-heptyl- and methyl-n-nonyl carbinols. The alcohols, together amounting to 12 %, were optically active and dextro rotatory [1]).

G. H. SALWAY [2]) found ± 1.1 % of volatile unsaponifiable constituents, consisting principally of methyl-nonyl ketone, in a sample of palm-kernel oil. This was confirmed by SCHIMMEL and Cie [3]), who detected also methyl-amyl- and methyl-heptyl ketones.

These fats and the nature of the ketones found corroborate the experimental results. It is, therefore, very probable that these various substances detected in coconut- and palm-kernel oils are formed by fungi. ORLA JENSEN's [4]) paper on the rancidity of butter shows that several investigators had unconsciously caused the formation of ketones in their experiments with fungi on fats. JENSEN demonstrated that when butter became rancid "esters" appeared (ethyl-butyrate,) this being in agreement with the results of AMTHOR [5]), who, however, found in addition to esters in rancid butter, other substances which were unsaponifiable. These were undoubtedly ketones. Two fungi in particular were responsible for the formation of "esters" (ketones):

1. Cladosporium butyri, ORLA JENSEN; This organism, according to my observations is not a cladosporium, but belongs rather to the group of saprophytic monilia; it forms real esters not only in butter, but also in nutrient media containing glycerine or carbohydrates.

2. Penicillium glaucum: [6]) This fungus did not produce „esters" in a culture medium, but did so when grown along with Oidium lactis on butter. This increased „ester" formation, noted also when Odium lactis and Cladosporium butyri were grown together, is no longer te be wondered at; Oidium lactis has powerful lipolytic properties and by reason of the marked formation of free fatty acids narcotizes Cladosporium butyri and Penicillium glaucum so that ketones are now formed. The following sentence by JENSEN is conclusive: "Die mit Penicillium geimpfte Butter roch nämlich bei der Distillation deutlich nach Amyl-butyrat und vielleicht auch nach Aethyl-butyrat." [7]) The odour of methyl-amyl ketone and that of amyl-butyrate are similar, but the odour of the ketone is the more ethereal. ORLA JENSEN also observes that lactose represses "ester" formation.

H. C. JACOBSEN [8]), who experimented with vegetable fats, confirmed the formation of "esters" by the action of fungi on coconut oil on the basis of JENSEN's work. Besides his Penicillium glaucum and Cladosporium butyri Orla Jensen, also Aspergillus spec., Mucor spec., Clasterosporium spec., Hormodendron spec., and Phoma spec. gave rise to the formation of „esters". Oidium lactis did not produce „esters".

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[1]) The carbinols are formed from the ketones by biological reduction. Cf. the reduction of methylnonylketone to dextro-rotatory methylnonylcarbinol by fermentation, by C. NEUBERG and F. F. NORD, Ber. **52,** 2237—48 (1919).

[2]) G. H. SALWAY, Journ. Chem. Soc. **111,** 407 (1917).

[3]) SCHIMMEL and Cie, Ref. Seifensieder Ztg. (1919) 496.

[4]) ORLA JENSEN. C.f. Bakt. II Abt. **8,** (1902).

[5]) AMTHOR. Zeitschr. f. Anal. Chemie (1899) p. 10.

[6]) Vide page 7, note 2.

[7]) ORLA JENSEN, loc.cit. page 369.

[8]) H. C. JACOBSEN, Folia Microbiologica, **5,** Part 2, (1918).

The investigation of W. N. STOKOE [1]) appeared in 1921. Though he did not explain the way in which ketone formation is brought about, he has been the first to explain the exact constitution of the products which cause this rancidity. He grew the fungi on an emulsion of coconut oil and gelatine lactose medium with the result that the formation of ketones took place only with coconut- and palm-kernel oils, not with butterfat. Contrary to JACOBSEN he found that only Penicillium and Aspergillus species produced "perfume rancidity" i.e. ketone formation. [2]) Botrytis cinerea, Mucor mucedo, Cladosporium oidium and Oidium lactis did not form ketones.

This discrepancy is no doubt due to the fact that JACOBSEN experimented on a poorer nutrient medium than that used by STOKOE, for it has been shown that Penicillium cyclopium and Penicillium Roquefort formed ketones only in an inorganic medium using coconut oil as the sole source of carbon, but grew without ketone formation in the saccharose-containing RAULIN-DIERCKX solution. JACOBSEN's results are supported by the following experiments in which different fungi were tested with regard to their ketone-forming capacity at a temperature of 23° C. using an inorganic medium in which coconut oil was the sole source of carbon. After a period, the length of which depended on the rate of development, the formation of ketones was demonstrated with the following fungi:

Penicillium leucopus Biourge, P. cyclopium Westling, P. flexuosum Dale, P. rubrum Stoll?, P. baculatum Westling, P. Roquefort Thom, P. brevi-compactum Dierckx, P. (Citromyces) Pfefferianum Wehmer, P. (Scopulariopsis) brevicaule Saccardo, Aspergillus glaucus (Link (?), Asp. minimus Wehmer (?), Asp. flavus Link, Asp. albus Wilhelm, Asp. niger van Tieghem, Asp. fuscus Bonorden (?), Cladosporium herbarum Link, Monilia Australica Derx nov. spec., Monilia (Cladosporium) butyri Orla Jensen, Sporodesmium spec., Trichoderma Koningi Oudemans (?), Hyalopus spec.

Formation of ketones was not observed in experiments with:

Penicillium italicum Wehmer, Oospora (Oidium) lactis Fresenius, Thielaviopsis ethacetica Went, Catenularia fuliginea Saito, and Penicillium digitatum Saccardo.

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[1]) W. N. STOKOE, Journ. Soc. of Chem. Ind. **40**, 75—81, (1921).

[2]) STOKOE is of opinion that from Penicillium cultures he has isolated an exo-enzyme which splits coconut-oil with formation of ketones. Some objections, however, may be raised against his method of procedure; up to this moment I have not yet succeeded in isolating such an enzyme. The views, mentioned above, on the narcotic action of fatty acids on the respiratory functions of the mycelium do not make the appearance of an oxidative exo-enzyme more probable.

Two groups of these fungi showing a negative reaction can be distinguished; 1. those showing hardly any growth under the experimental conditions, and which need therefore no discussion, and 2. those growing well under the same conditions. To the latter group belong Penicillium italicum Wehmer, and Oospora lactis Fresenius. No doubt the conditions are still too favourable in this case, for if Penicillium italicum is grown in a RAULIN-DIERCKX solution, containing saccharose and to which $^1/_2\,^0/_0$ of potassium caproate is added, formation of methyl-propyl ketone is observed. Under these conditions Oospora lactis does not grow at all.

Thus there is only a quantitative difference between these fungi as regards their ketone-forming capacity. With the exception of Oospora lactis in every case ketone formation could be experimentally demonstrated. Not can it be attributed to chance that Oospora lactis is an exception; its very vigorous fat-splitting and oxidizing properties are well known. The organism also appears to offer a strong resistance to antiseptics [1]). These facts give a better insight as to the reason of the non-ketone-forming capacity of Oospora lactis.

It is a remarkable fact that the above mentioned ketones occur naturally in other substances; the ethereal oil from Ruta graveolens consists to the extent of $90\,^0/_0$ of a mixture of methyl-nonyl- and methyl-heptyl ketones; the ethereal oil from the leaves of Citrus limetta also contains methyl-nonyl ketone. Methyl-amyl ketone is present in the ethereal oil from the bark of Cinnamoneum Zeylanicum and in the oil from the flower-buds of Eugenia caryophyllata. And these are precisely the ketones formed by fungi, e.g. from coconut oil. The probability is therefore enhanced that they are formed in the same way in plants, i.e. by imperfect oxidation of fatty acids. Finally we may point to the chemical analogy of this reaction viz. the demonstration by DAKIN [2]) that methyl ketones are formed when the ammonium salts of fatty acids are treated with hydrogen peroxide. In this purely chemical process, too, the oxygen attacks the molecule at the $\beta$-position.

## SUMMARY.

1. Stress is laid upon the great analogy existing in the fermentative and oxidative processes of microorganisms, higher plants and animals.

2. The formation of methylketones in the cleavage of fatty acids by fungi proves that in this case also oxygen attacks the $\beta$-carbon atom.

3. The fatty acids, up to and including myristic acid, are adsorbed on the mycelium of fungi, and exert a more or less depressing effect on their respiratory functions. This is the reason the oxidation of these fatty acids cannot extend beyond the corresponding ketonic acids, which, at this point, perhaps under the influence of a carboxylase, decompose into carbonic acid and a methylketone. At the same time it follows that the formation

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[1]) Vide LAFAR, Handb. d. Techn. Mykologie, IV, 344, Jena (1907).

[2]) DAKIN, Journ. of biol. Chem. 4, 221, 227, 225 (1908).

of ketone only appears under unfavourable conditions. The ketones are not normal intermediate products in the oxidative cleavage of fats.

4. Almost all fungi can form ketones, the only exception so far found being Oospora lactis; probably this is to be attributed to the very vigorous oxidizing properties of this fungus.

5. In fungi, as in the higher animals, the process of the oxidative cleavage of fats is analogous. As the same methylketones are found in different ethereal oils this process probably takes the same course in plants also.

*Delft,* June, 1924.

**Chemistry.** — "*The Influence of Pressure on the Solubility of Substances V. The system Naphtalene-Tetrachlorethane*". By Prof. ERNST COHEN, WILHELMA A. T. DE MEESTER, and Dr. A. L. TH. MOESVELD.

(Communicated at the meeting of October 25, 1924).

1. The investigations [1]) on the influence of pressure on the solubility of substances have taught that this influence is relatively small, compared with the effect of temperature. Yet a few cases are known in which the effect of pressure is very considerable, and so the question arises: how does in these cases the solubility depend on pressure?

Theoretical considerations, to which we shall revert directly, show that great effects are to be expected only in those cases in which pressure diminishes the solubility. Considering that the decrease with increasing pressure must become smaller, the question arises, whether the solubility will pass through a minimum, or with increasing pressure will asymptotically approach a definite value.

In one of our former investigations [2]) it was shown that the results of the determinations of solubility could very well be represented by a parabolic curve, so that the existence of a minimum could be made plausible. This, however, lay outside the range investigated experimentally. As, moreover, it would occur at a pressure more than twice as great as the highest at which measurements had been carried out, great value cannot be attached to this extrapolation. So it was of importance first of all to find a system of substances which was more suitable for such an investigation.

2. Two ways are open to find such a system: If it is possible to find by a theoretical method the conditions which must be satisfied in order to get a strongly curved solubility curve, such a case can be investigated directly. As, however, the curving of this line depends i.a. on the compressibilities of the solute and the saturated solution, and data on this subject as regards the solute, don't practically exist, while the determination of these values takes much time, and so does not lend itself at all

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[1]) Zeitschr. f. physik. Chemie **67**, 432 (1909); **69**, 102 (1909); **75**, 257 (1910); **93**, 385 (1919); **94**, 210 (1920); **104**, 323 (1923); **105**, 155 (1923); Journ. Amer. Chem. Soc. **38**, 2632 (1916). Thesis CASTEELS, Neuchatel, (1920).

[2]) Zeitschr. f. physik. Chemie **93**, 385 (1919), especially page 433 et seq.

to preliminary investigations, we have followed the second method, which leads us to find systems in which pressure has great influence on the solubility.

In such a case the solubility curve must soon curve when the pressure is increased, as otherwise negative values of solubility would have to appear. In order to find such systems it is only necessary to determine the fictitious change of volume which accompanies the process of solution, for which several different methods are at our disposal [1]). But even in those cases, in which the influence of pressure on the solubility is slight, a minimum may be expected, as the same curvature of a curve directed slightly downward, makes the curve slope upwards again at a much smaller pressure.

3. If we do not take into consideration the complications which arise when the vapour of the saturated solution does not follow RAOULT's law, we may write:

$$\frac{d\,l.c}{dp} = -\frac{\Delta v}{RT}$$

in which $c$ is the concentration of the substance dissolved in mol. $^0/_0$, $p$ the pressure, $T$ the temperature, $\Delta v$ the fictitious change of volume at $T$ and $p$, and $R$ the gas constant.

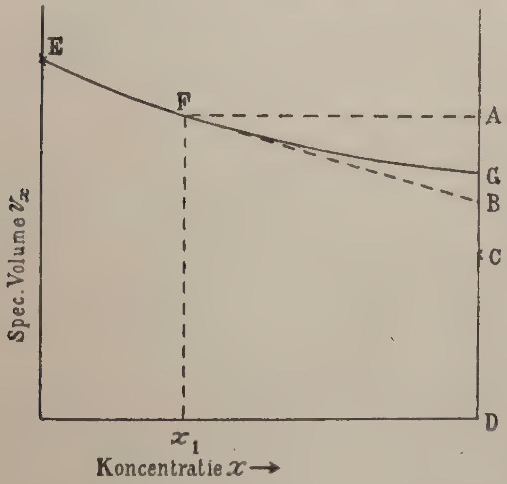

Fig. 1.

The form of the curve which represents the solubility as function of the pressure is now determined by the value of $\Delta v$ as function of the pressure:

$$\frac{d(\Delta v)}{dp} = \frac{\partial(\Delta v)}{\partial p} + \frac{\partial(\Delta v)}{\partial c}\frac{\partial c}{\partial p}.$$

The first term of the right hand of the equation represents the change which $\Delta v$ undergoes with pressure as a consequence of the difference in compressibility of the solid and its melt (assumed to be in a subcooled state). The second term relates to the change with pressure (and the concentration) of the volume change on mixing the solvent and the solute (subcooled). This is easily seen in Fig. 1 [2]). For, at a higher pressure, the curve $EFG$ as well as the point $C$ lie lower. Moreover $EFG$ does not remain parallel to itself, while the point $F$ is also displaced.

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[1]) Zeitschr. f. physik. Chemie **105**, 145 (1923).

[2]) See concerning this figure also Zeitschr. f. physik. Chemie **93**, 385 (1919), especially par. 66.

If we assume, as a first approximation, that $\triangle v$ is a linear function of the pressure:

$$\frac{d l.c}{dp} = \alpha + \frac{\beta p}{RT}$$

or at constant temperature:

$$\frac{d l.c}{dp} = A + Bp$$

$$l.c = Ap + \frac{B}{2} p^2 + C.$$

Depending therefore on the sign and the value of the coefficients there is a possibility for a minimum in the solubility. However, it is also possible that the solubility curve runs asymptotically. If we pay attention only to the influence of the compressibilities on the value of $\triangle v$ it is highly possible that $\triangle v$ does not depend lineary on pressure, but approaches to zero when the pressure increases. The investigations of BRIDGMAN [1]) have shown that the change of volume on melting (this, however, is only one term of $\triangle v$, unless the process of dissolving in the saturated solution occurs without contraction) seems to tend to zero with increasing pressure. Here, however, the temperature is not constant, but increases with the pressure.

4. When investigating the fictitious volume change during solution our attention was especially drawn to the system naphtalene-tetrachlorethane [2]). It seemed to us that this system was extremely suitable for an investigation on the influence of pressure on the solubility. For, in this case, not only $\triangle v$ is great, but at the same time a very simple method can be applied here for the determination of the composition of saturated solutions. By a pycnometric method the specific volume of these solutions is determined.

In order to determine the solubility curve under pressure, the method followed was a direct one, a modification of the one which we had used previously, when investigating the system *m*-dinitrobenzene-ethylacetate. As the solution of naphtalene in tetrachlorethane assumes a dark colour, when it is in contact with the iron wall of the pressure-bomb, it was necessary to shake the solutions in a glass vessel. When the solution equilibrium had been reached under pressure, the saturated solution under equilibrium-pressure was forced from the glass vessel in the bomb, into some pipettes. From these pipettes the solution, (saturated at $t^\circ$ and $p$ atm.) was pressed into a pycnometer, in order to determine the specific volume of the solution. The concentration could be calculated by means of the equation previously found, which gives the relation between the specific volume and the concentration.

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[1]) Physical Review, N.S. **6**, 94 (1915).

[2]) Zeitschr. f. physik. Chemie **108**, 103 (1924).

### *The materials used.*

5. The tetrachlorethane and the naphtalene used in this investigation were prepared and purified in the same way as has previously [1]) been described by us.

### *Apparatus and Experimental Method.*

6. The shaking bomb (Fig. 2), the thermostat, the piezostat, manometer, and pressure gauge, as well as the thermometers have already previously been described by us [2]). The shaking bomb was the same that had been used in our investigation on the influence of pressure on the solubility of thallous sulphate; the steel rod *K*, however, had been replaced by a shorter one, in consequence of which there was more space for mercury in the limb *A* of the bomb, so that a greater quantity of liquid could be driven out of the other limb, by pressing oil into *A*.

7. The solubility pipette used in this case consisted of a tube *A* (Fig. 3) drawn out at the lower end into a capillary *B*, and provided at the top with a carefully ground stopper *C*, fitting closely on *A*, by means of RAMSAY lubricant. During the shaking of the pipette in the bomb the stopper *A* was kept down by means of two perforated iron plates (*D* and *E*), connected with each other by thin iron wire *G*, *G*, as is shown in the figure. The spiral *F* keeps the wires stretched. During the shaking the capillary *B* is plunged in a glass tube *H*, filled with mercury. The tube is closed with a cork, provided with a slit, through which the mercury of the bomb can pass.

The filling of the pipette, in order to carry out a determination, was done in the following way: The pipette *A* is closed at *B* with a finger. One or two cc. of mercury are put in, and then it is nearly completely filled up with a solution of naphtalene in tetrachlorethane, which, at the pressure at which the investigation will be made, is still unsaturated. Moreover so much solid naphtalene is added, that after reaching the pressure equilibrium "Bodenkörper" is present. The pipette is closed with *C*, so much of the solution is added, that the stopper is also filled with it, and the spiral, the iron plates *D* and *E*, as well as the iron wires are put in place.

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[1]) Rec. Trav. Chim. d. Pays-Bas **42**, 779 (1923); Zeitschr. f. physik. Chemie **108**, 103 (1924), especially p. 105.

[2]) Zeitschr. f. physik. Chemie **104**, 323 (1923).

Meanwhile the stopper *E′* (Fig. 2) of the shaking bomb with the cock *H*, has been put upside down between the edges of two tables, and the capillary *G* (*H* is closed) completely filled with mercury. In the part of the capillary which is now directed upward a plug of cottonwool is inserted, and a piece of thick-walled rubber tube has been shoved over the capillary. This is also filled with mercury and is connected with the glass bulb *K* which is also filled with mercury. The glass bulb enables us to keep the capillary filled with mercury during shaking, and prevents the solution from coming into contact with iron. If this is not carefully seen to, not only impurities will appear in the solution, but at pressures above 750 atm. the solution will be driven out of the tap *H*. When placing the bulb on the india-rubber connexion it must be turned in such a way that, during shaking, when the pipette *A* is pretty well horizontal, the opening *K* of the tube *L* is continually directed upward. Should any of the solution enter the bulb during shaking, it will be left there [1]), as there is always mercury in the tube *L*, so that the solution can never enter the tap.

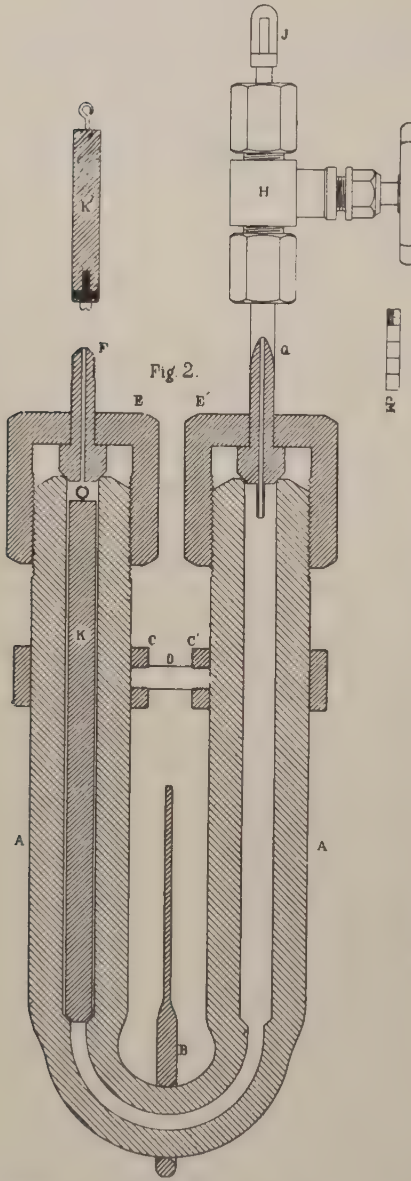

Fig. 2.

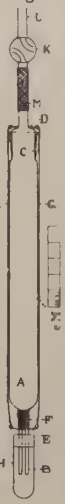

Fig 3

When the solution is tapped, — pipette and bulb are now placed in a vertical position —, it can leave the bulb through *K* and *L* unimpeded; the mercury in *G* (Fig. 3) is sometimes driven out as first fraction, sometimes replaced by the solution, and then also sinks into *K*.

In the tube *M* a thick plug of cottonwool is placed, a piece of thick walled rubber tube is shoved over *M* and the pipette *A* is connected with $M$. If the tap with the pipette is now turned 180°, the pipette hangs on the tap. By means of the cork, $B$ is placed on the cup $H$ filled with mercury. When a certain quantity of mercury has been poured into the limb $A'$ of the bomb, the pipette is allowed to sink into this limb, but care is taken that the mercury stands as high as the upper rim of this leg, before the cap $E'$ is screwed on to this limb. In order to get $A'$ filled with mercury up to the brim, when the pipette is lowered into this limb, a steel rod $K'$ is inserted into the limb $A$, of about one half the length of the rod $K$ drawn in the figure. At the bottom this rod is provided with a leather disc. It can move in the limb $A$ like a well fitting piston, which drives the mercury into $A'$, and makes it rise in it, until it reaches the brim at the top. The quantity of mercury present in the bomb, must be such that the rod in $A$ ends just below the upper rim of $A$. The rest of the remaining space of $A$ is filled up with oil. Then $A$ is closed with $E$.

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[1]) During shaking the lower half of the bulb, into which *L* opens, will always remain filled with mercury.

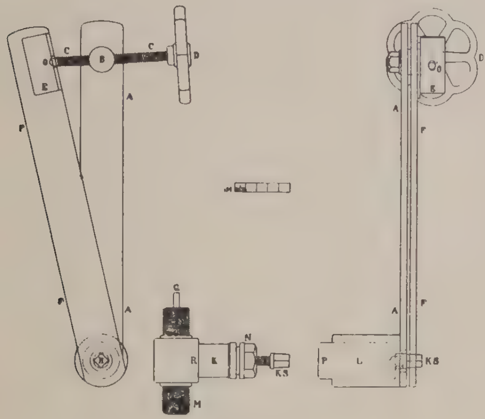

Figure 4.

8. Now the shaking bomb is lowered into the thermostat, the limb $A$ is connected with the pressure capillary, and the motor, which keeps the bomb in motion, is set going.

9. Usually the shaking was continued for eighteen hours, from the afternoon until the following morning. Intensive stirring is due to the mercury which had first been put into the pipette, plus the quantity which enters during the compression of the solution. Moreover the solid naphtalene floats in the solution, so that stirring is not impeded, even when there is a great excess of solid substance.

10. In order to get from the pipette samples of the saturated solution for analysis we proceed as follows: The motor is stopped, the bomb being in a vertical position. After removing the glass cap, which prevented the steel tube $J$ from being soiled by oil from the thermostat, a tube of india rubber is shoved over this steel tube $J$. Connected with the india rubber tube is a pipette, the body of which can be closed by two stop-cocks. Then the tap $H$ is opened very slowly by means of a key which has been especially constructed for this purpose. Care is taken to keep the pressure in the bomb unchanged, which is done by a supply of oil into the bomb by means of the pressure pump of the piezostat,

which in this case is worked by hand. The special key (see Fig. 4) consists of two levers *A* and *F*, of which *A* is fixed, and *F* can be moved very gradually by means of the wheel *D*, which can turn the screw *CC*, and so opens the tap *K* very slowly.

As it was found that, when tapping, a certain quantity of naphtalene was always deposited — especially at the spot where the transition from high pressure to 1 atm. takes place — and as there was only a rough agreement in the concentrations found of parts of the solution which were tapped consecutively, we have tried to find the cause of this phenomenon. It was found that it is to be attributed to the cooling which manifests itself at the spot where transition from high pressure to 1 atm. takes place. It was proved that naphtalene, carried along mechanically, (the solute in this case is lighter than the saturated solution) was not the cause of this phenomenon, for it showed itself also when the pipette was filled with an unsaturated solution, and solute was present in the shape of small cast bars, sewn in linen bags.

In the concentration of different parts of the tapped, saturated solution a very good agreement was found however, when during tapping a current of warm air blew against the part *H* of the tap. This current was obtained by means of a so called „Fön", an instrument which is used by hairdressers in drying hair. We connected it up with the electric lighting net (220 Volt), in series with a lamp resistance, so that the current of air had a temperature of 50° C. There was no dissolving of solute during the heating; the plugs of cottonwool prevented the solid naphtalene from rising higher than the bottom of the glass bulb, while the bomb itself is immersed in the oil of the thermostat, almost as far as *H*, during tapping, so that it is not influenced by the warm current of air.

After drawing some cc. of first fraction, we usually tapped the saturated solution consecutively in different pipettes, every time 8 cc.

11. We determined the concentration of these saturated solutions by determining the specific volume at 30°.00 C. In the obliquely drawn out part of the pipette a plug of cottonwool was placed, and this part was connected by means of an india rubber tube with a pycnometer (capacity 6 cc.) according to SPRENGEL-OSTWALD-HOLLEMAN [1]). To the second stem of this pycnometer a small tube was fixed, and a small bellows to the open end of the pipette. The pycnometer and the pipette are now plunged in a thermostat (30°.00 C.) provided with windows, and both cocks of the pipette are opened, when the whole apparatus has taken on the temperature of the thermostat (after about 15 min.). The saturated solution is pressed slowly into the pycnometer. If it is nearly entirely filled, the tube on the limb of the pycnometer farthest from the pipette

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[1]) Rec. Trav. Chim. d. Pays Bas **13**, 24 (1894); **19**, 79 (1900).

is removed, and this limb is almost quite closed with a finger. If this method of procedure is followed it is impossible that water from the thermostat enters the pycnometer, in consequence of the air escaping from it. As soon as the solution has reached the beginning of the graduation of the limb of the pycnometer, this limb is quite closed with the finger, and the connection of the other limb with the pipette is broken. Then the pycnometer is taken out of the thermostat, and held in such a position, that the solution in both limbs can be read somewhere on the scale.

Now the pycnometer is again immersed in the thermostat, one capillary is quite closed with a finger, and we wait until the apparatus has assumed the temperature of the thermostat, which is seen from the constant position of the meniscus in the open limb.

The pycnometer is now dried and weighed. From the data obtained the specific volume of the saturated solutions is calculated, and their concentration is found by means of the equation (see § 4).

## *Results.*

12. When the preliminary determinations were made, we were led to expect, that it would be possible to continue the measurements up to 1500 atm. The final determinations, however, showed us, that, when at pressures up to 1000 atm. samples of the saturated solutions were tapped in three parts, the agreement in the concentrations of these parts found was very satisfactory, and also when such a test was repeated at the same pressure. This agreement disappeared however at 1250 and 1500 atm. Probably this is to be attributed to the rapid increase over 1000 atm. of the viscosity of the oil which transmits the pressure in the capillary (length 12 M.), which connects the shaking bomb with the piezostat.

An improvement was obtained when lighter oil was used, but the agreement above 1000 atm. was so much worse than the agreement below that pressure, that we shall not consider here the determinations made above 1000 atm.

The great viscosity of the oil causes, when the solution is tapped, a totally different pressure near the tap where the solution flows out, than near the pressure pump, and the manometer indicates the latter pressure.

We hope to construct an apparatus later on, in which the disturbance just mentioned will be eliminated. In this paper we shall consider only such results as have been obtained up to 1000 atm.

Table 1 contains these results.

For computing an interpolation formula which represents the observations we have used the type:

$$c = \alpha + \beta p + \gamma p^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

as well as the form:

$$\log. c = \alpha_1 + \beta_1 p + \gamma_1 p^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

TABLE 1.

Determinations of solubility in the system Naphtalene-Tetrachlorethane.
(Temp. 30°.00 C.).

| Number of the Experiment | Pressure in atmospheres | Concentration (in gms. per 100 gms. of solution) of the three tapped parts. | | | Mean concentration (in gms. per 100 gms. of solution) |
|---|---|---|---|---|---|
| 1 | 0 | 35.07 | | 35.07 | 35.07 |
| 2 | 250 | 30.24 | 30.23 | 30.25 | 30.26 |
| 3 | 250 | 30.29 | 30.29 | 30.25 | |
| 4 | 500 | 26.43 | 26.41 | 26.43 | 26.40 |
| 5 | 500 | 26.37 | 26.39 | 26.39 | |
| 6 | 750 | 23.34 | 23.36 | 23.31 | 23.33 |
| 7 | 750 | 23.33 | 23.30 | 23.32 | |
| 8 | 1000 | 20.86 | 20.92 | 20.82 | 20.89 |
| 9 | 1000 | 20.89 | 20.89 | 20.96 | |

in which $c$ in both cases represents percentage by weight (solvent = 100, also solution = 100) as well as molecular percentage.

In every case the divergencies between the values found of $c$ and those computed from the equations, where greater when the equation type 1 was used than with type 2, especially when $c$ was expressed in percentages of weight of the solvent.

For illustrative purposes we shall in one of the cases also mention the values which were obtained with the equation type 1.

If the concentration is expressed in moles of naphtalene per 100 moles of solution, we find by means of the method of least squares:

$$log.\, c = 1.61764 - 0.24196 \,.\, 10^{-3}\, p + 0.03432 \,.\, 10^{-6}\, p^2 \quad . \; . \quad (a)$$

If we use percentage of weight we find in the same way:

$$log.\, c = 1.54504 - 0.26840 \,.\, 10^{-3}\, p + 0.0432 \,.\, 10^{-6}\, p^2 \quad . \; . \quad (b)$$

and if $c$ is expressed in percentage of weight (solvent) = 100):

$$log.\, c = 1.73224 - 0.39974 \,.\, 10^{-3}\, p + 0.0895 \,.\, 10^{-6}\, p^2 \quad . \; . \quad (c)$$

and for the other type of equation:

$$c = 53.85 - 44.74 \,.\, 10^{-3}\, p + 17.46 \,.\, 10^{-6}\, p^2 \quad . \; . \; . \; . \quad (d)$$

Table 2 gives a survey of the (mean) values found, and of the values calculated by means of the equations (*a*—*d*). In the equations (*a*), (*b*), and (*c*) the probable error of a calculated concentration is respectively about 0.03, 0.02, and 0.05 %.

Though the agreement between the values found and those calculated

TABLE 2.

Determinations of solubility in the system Naphtalene-Tetrachlorethane.
(Temp. 30°.00 C.)

| Pressure in atmospheres | Mole percentage | | Weight perc. $\Sigma=100$ | | Weight perc. solvent $=100$ | | |
|---|---|---|---|---|---|---|---|
| | found | calc. (*a*) | found | calc. (*b*) | found | calc. (*c*) | calc. (*d*) |
| 0 | 41.45 | 41.46 | 35.07 | 35.08 | 54.01 | 53.98 | 53.84 |
| 250 | 36.25 | 36.25 | 30.26 | 30.24 | 43.39 | 43.44 | 43.75 |
| 500 | 31.94 | 32.01 | 26.40 | 26.40 | 35.87 | 35.87 | 35.84 |
| 750 | 28.51 | 28.54 | 23.33 | 23.34 | 30.43 | 30.39 | 30.11 |
| 1000 | 25.71 | 25.70 | 20.89 | 20.89 | 26.41 | 26.42 | 26.58 |

by means of the equations (*a*), (*b*), and (*c*) is very satisfactory, it again appears how uncertain such equations are when we want to extrapolate. If the pressure is computed, at which a minimum of solubility would appear, the equations (*a*), (*b*), and (*c*) give respectively the values $p=3500$, 3100, and 2200 atm.

So, from the figures found in this case, it would be premature to draw the conclusion that, at increased pressure, the solubility passes through a minimum.

Finally we wish to point out that the system under consideration gives another example of the great influence which pressure can have on solubility. For the first 250 atm. of increase of pressure, the decrease of solubility amounts to about 10.5 % calculated per 100 gms. of solvent. Moreover the divergence from RAOULT's law is, in this case, exactly the opposite of the divergence in the system *m*-dinitrobenzene-ethylacetate. With this system the influence of pressure on solubility was greater than would result from the value $\triangle v$. In our case the value of $\triangle v$, directly determined [1]), was 0.1313 cc./gm, whereas the pressure coefficient of solubility for 0 atm. gives $\triangle v = 0.1082$, according to the equation:

$$\frac{dl.c}{dp} = -\frac{\triangle v}{RT},$$

which holds good if the solution follows RAOULT's law, in connexion with the equation (*a*), and with $R=82.07$, $T=303.09$, l.c. $=2.305$ *log. c*, and the value of the molecular weight of $C_{10}H_8 = 128.06$.

While, when RAOULT's law holds good,

$$(1-c)\left(\frac{\partial l.p'}{\partial c}\right)_T = -1$$

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[1]) Zeitschr. f. physik. Chem **108**, 103 (1924).

(in which $p'$ represents the vapour pressure of the saturated solution) this factor has now the value of — 1.21. Consequently the vapour pressure of the saturated solution is smaller, the decrease of vapour pressure greater than would be computed from the concentration, when RAOULT's law holds good.

## *Summary.*

The solubility of naphtalene in tetrachlorethane was investigated at 30°.00 C. and at pressures of 1—1000 atm. A minimum in the solubility curve, which seemed possible on the strength of analogous investigations, could not be established in this system within this interval of pressure.

*Utrecht*, October 1924. VAN 'T HOFF-*Laboratory*.

**Chemistry.** — *"On Disaccharins."* (Second preliminary communication.) By H. J. CHOUFOER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated at the meeting of December 27, 1924)

## *Disaccharins from M-Xylene.*

As was already communicated[1]) through oxidation of 1, 3-xylene, 4,6 disulphanide a product is obtained which melts at 268°—270°. Its N-content was 9,8 $^0/_0$, while 9,7 $^0/_0$ is required for a diimide.

No diminution of weight could be observed even on prolonged heating at 140°.

Like WISCHIN I took this product for a disaccharin.

To get more certainty I have tried to titrate this substance. On use of the indicator phenolphtaleine the change of colour is indefinite. Of course carbonic acid free lye and acid were used. For the eq. weight 213 was found. The eq. weight of a diimide is $\frac{288}{2} = 144$. When only one of the $CH_3$-groups is oxidized, the substance has the eq. weight of 277 or 295 according to whether or no water has been split off. Accordingly my result does not correspond to any of these compounds.

This deviation may be accounted for in different ways. In the first place it may be assumed that a diimide is a very feeble acid. In the second place the possibility exists that the product is a mixture of the said compounds. In the third place it is possible that only one of the $CH_3$-groups is oxidized, but that also the $SO_2NH_2$-groups consume part of the lye.

In fact, a good deal of lye appeared to be required to neutralize the disulphamide with respect to phenolphtaleine. The change of colour was very indefinite.

The indicator methylred appeared not to be affected by the diamide. Hence the titration was repeated with methylred as indicator. The colour change was definite. The value of 290 was found for the eq. weight.

It may now be considered as certain that only one of the $CH_3$-groups has been oxidized. The product described, which after some crystallisations crystallizes in short, thick, transparent prisms, and possesses the melting-point of 272°, has, therefore, one of the subjoined structures:

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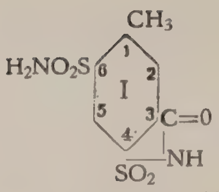
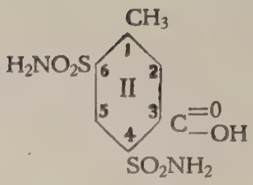
[1]) These Proceedings, 27, p. 353.



N=10.1 $^0/_0$



N=9.5 $^0/_0$

When $BaCO_3$ is added to the solution of this body, it is transformed into the Ba-salt with generation of $CO_3$, which Ba-salt is readily soluble. In this respect it strongly reminds of a sulphonic acid.

Ba weight 19,11 $^0/_0$.

Cal. I 19,83 II 18,84.

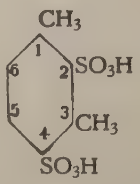
Hence structure II is probably the correct one.

When the diamide is oxidized with the quantity of $KMnO_4$ calculated, or rather $1^1/_3 \times$ the quantity calculated, a precipitate is formed on acidification which consists partly of unchanged diamide, but chiefly of the acid II described above.

If the solution is evaporated after filtration, and when the salt-mass is extracted with alcohol, a hygroscopic mass is left after evaporation of the alcohol. This mass was dissolved in water. The solution gives rise to generation of carbonic acid gas with $BaCO_3$. When the solution is evaporated, a Ba-acid is obtained, which remains viscid even after drying in an exsiccator. If, however, it is boiled out with alcohol, it forms a white powder, which no longer attracts water. It produces no reaction with $AgNO_3$ on solution in water, accordingly there is no $BaCl_2$ present. A barium determination yielded 23,8 $^0/_0$. The Ba-content is, therefore, considerably higher than of the mono-basic acid. We have possibly here a mixture in which the barium salt of a disaccharin is present.

On further oxidation of the mono-basic acid with $KMnO_4$ in aqueous solution, part is recovered unchanged after acidification. In the way described some of the hygroscopic product may be again obtained. In this case the evaporation of the alcohol is followed by a small crystallisation melting at 112°—114°.

On direct sulphonation of M-xylene there is formed a by-product discovered by PFANNENSTILL, which, as was stated before, probably possesses the structure



To obtain somewhat more of this by-product, I have carried out the sulphonation at higher temperature. Apparently a great quantity of oily disulpho-chloride is then obtained.

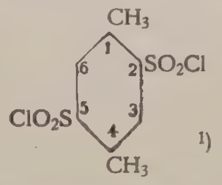
A large part of the 1,3-xylene-4,6-disulpho-chloride, however, remains liquid, in consequence of the formation of resin.

This oil must then be transformed into the amide, and it is very difficult to isolate the diamide from the by-product. After purification the melting-point is 235°. The melting-point of the mixture with 1,3-xylene-4,6 disulphamide presents a deep depression.

After oxidation with $KMnO_4$ addition of acid causes only a slight deposition of a precipitate, which appears to be the K-salt of an org. salt. Possibly we may have to do here too with an easily soluble product of oxidation.

*Di-saccharins of p-xylene.*

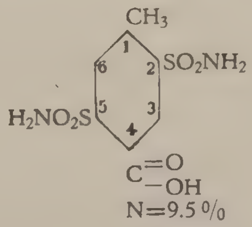
In the direct sulphonation of p-xylene there are formed two di-sulpho chlorides. The by-product possesses a melting-point of 162°, and as I have proved by synthesis, it has the structure:



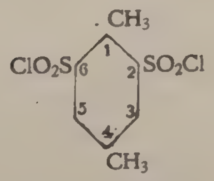
On oxidation the amide prepared from this yielded a product with a melting-point of 320°.

On titration with methyl red as indicator the eq. weight appeared to be 301,3. Here, too, only one methyl group was oxidized.

A whole series of N-determinations gave a mean of 9.4 %, which points to the structure



As appears from the following synthesis, the structure of the main product is



The product started from is p-xylene.

On continued nitration 2 dinitroxylenes are formed[2], viz.:

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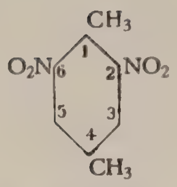
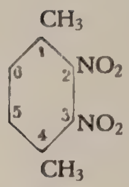
[1] Loc. cit.

[2] Ber. 19, 144.





which could not be separated by crystallisation in spite of persistent attempts. The mixture was partially reduced by boiling with $(NH_4)_2S$.

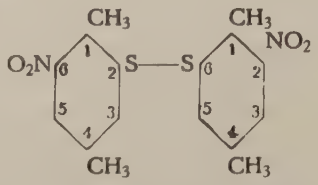
I. It is then converted to a nitroxylidine. Melting-point 96.

II. It becomes a black, tough, resinous mass, insoluble in acid.

On diazotation with $Na_2S_2$ the nitroxylidine from I passes into an orange compound, which admits of filtration, explodes in dry condition and becomes a tough brown mass with aromatic smell.

The orange compound still contains the nitrogen and can be rid of it by being slowly heated on a waterbath stirred with water.

At the ordinary temperature the brown compound is now as hard as stone; it has the structure



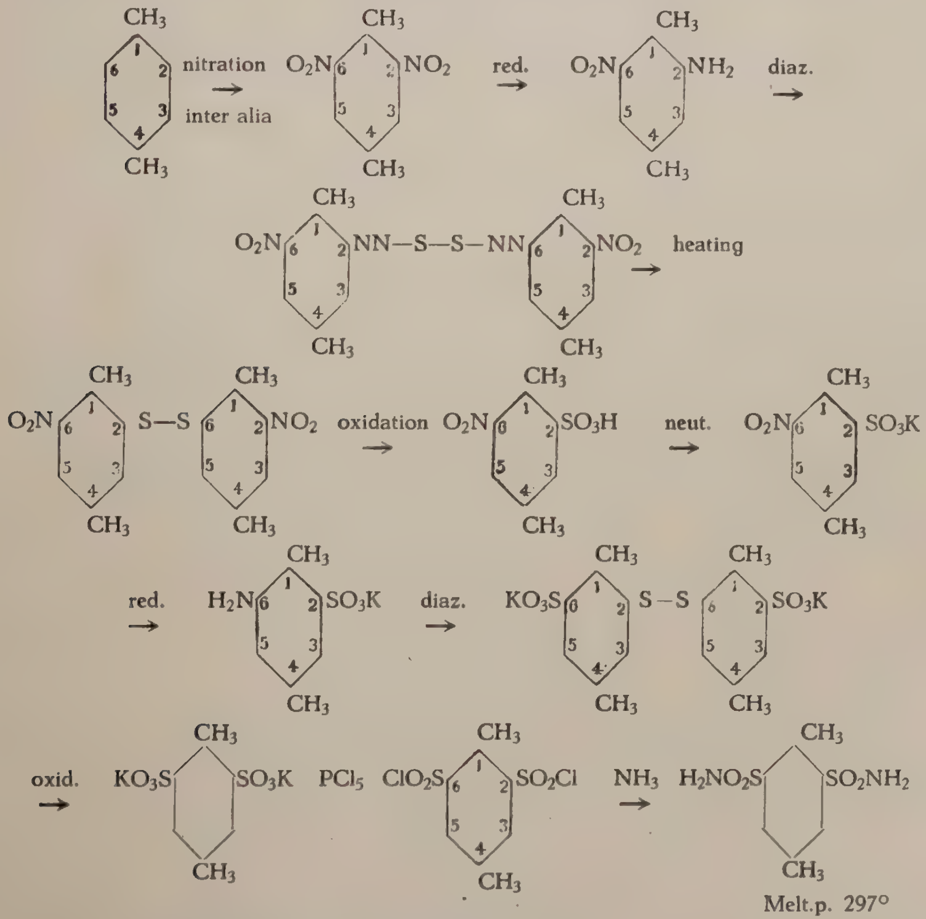
as to every grammolecule of nitroxylidine only $^1/_2$ gramme molecule of $Na_2S_2$ need to be added.

The brown di-sulphide is oxidized by fuming nitric acid with violent generation of heat already at the ordinary temperature. For this reason the more moderate oxidation with nitric acid Sg. 1.4 was preferred. The di-sulphide was, therefore, slowly heated on the water bath with nitric acid. The oxidation takes place near the boiling-point of nitric acid. The substance goes into solution, which is attended with generation of brown $NO_2$ vapours. Only a slight quantity of a brown crystallized substance remains behind. When, however, the solution is diluted with water, a larger quantity of a resinous substance is precipitated. Now the solution is distilled off in vacuum. This operation is four times repeated always after addition of water.

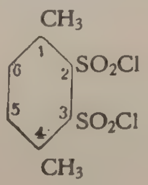
Then the distillate no longer reacts acid. The liquid is then neutralized with KOH. When the liquid has become slightly alcalic, the colour changes from light yellow to brown. After evaporation of the water the K-salt is changed with $PCl_5$ to the sulpho-chloride. When it is poured on ice, a brown solid substance separates. By a few times repeated recrystallisation of this substance from petroleum-ether large pale yellow monoclinic crystals are obtained, which melt at 61°.

The analysis agrees with the nitro sulphochloride of a xylene. Again the potassium salt of 1,4-xylene-2-nitro-6-sulphonic acid was prepared, but now reduced by boiling with $(NH_4)_2S$. By means of the diazotation method described the $NH_2$-group was replaced by the $SO_3H$-group, and the K-salt of the di-sulphonic acid obtained was converted with $PCl_5$ into the di-sulphochloride.

As the di-sulphochloride did not crystallize even after a few days' standing, I have changed it into diamide. The diamide was brown. This colour vanished immediately by boiling with alcohol, and the white diamide could be filtered off. Like the diamide of di-sulphonic acid, which constitutes the main product of the direct sulphonation of P-xylene, it melts at 297°. A mixing experiment with the diamide of the by-product shows depression. Hence the synthesis can be represented diagonatically as follows.

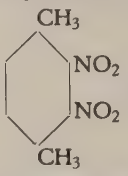

nitration
inter alia
red.
diaz.
heating
oxidation
neut.
red.
diaz.
oxid.
PCl5
NH3
Melt.p. 297°

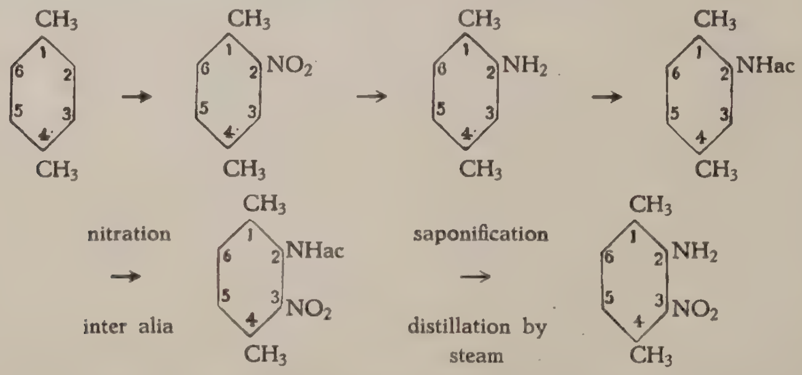
Then the synthesis of the di-sulphochloride



was taken in hand by me.

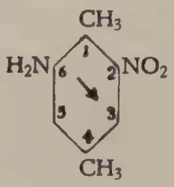
Evidently this compound does not arise on direct sulphonation of P-xylene; it is however, of importance for the synthesis of a disaccharin.

The before mentioned reduction product of  was a resinous mass, and could not be used as starting-point. In pure condition the nitro-xylidine was prepared according to a known method.

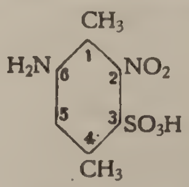


A clear almost colourless oil distilled over, which becomes solid when cooled on ice. This pure compound also appeared to be insoluble in acid, hence unfit for diazotation. Nor is this compound dissolved even by hot nitrous sulphuric acid.

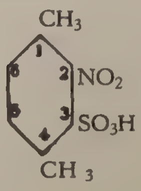
Another possibility of getting the groups at their right places was the sulphonation of



As the $NH_2$-group is strongly para-directive, the product expected was:



which by ontamidation would have to be changed into:



Neither at the ordinary temperature, nor at higher temperatures the nitroxylidine was attacked either by fuming sulphuric acid or by chlor-sulphonic acid. On heating with an excess of chlor-sulphonic acid at 180° for three hours a considerable carbonisation set in, but part of it was recovered unchanged.

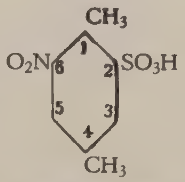
Then followed an investigation of the sulphonation of nitro-xylene. This is dissolved in fuming sulphuric acid, but it is not sulphonized at the ordinary temperature. By prolonged heating at 110° there enters a sulpho-group into the nucleus.

The sulphochloride was prepared in the ordinary way. This appeared to be complex, since it presented a melting-range.

By continued fractionated crystallisation from petroleum-ether I succeeded in separating 2 isomer nitro-sulphochlorides, which occur in the mixture in about equal quantities.

1. melting-point 74.5
2. „ 61.

The substance melting at 61° appeared to be identical with

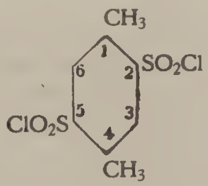


For a further examination the mixture of K-salts was reduced, and changed into the di-sulpho-chlorides by diazotation.

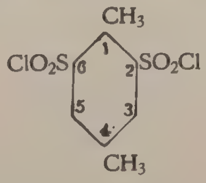
The mixture of di-sulpho-chlorides is liquid. Soon large crystals separate out of the solution in chloroform, melting-point 157°.

After recrystallisation the melting-point is 162°.

The substance was identical with

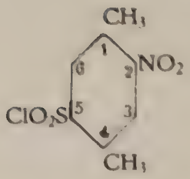


After a few days also needles separate out of the solution in chloroform, melting-point 72. These appeared to be identical with:



Here, too, the quantity of the isomers was about equal.

The first nitro-sulpho-chloride melting-point 74°.5 has, therefore, the structure:



Finally it remained to study the nitration of P-xylene-sulphonic acid. Para-xylene-sulphonic acid is not attacked by nitric acid sp.gr. 1.4, it is attacked by fuming nitric acid or in sulphuric acid solution with the calculated quantity of nitric acid.

The solution in fuming nitric acid was diluted, and the nitric acid was distilled off in vacuum. The K-salt was changed into the nitro-sulpho-chloride with $PCl_5$. The solution in ether yielded a crystallisation with the melting-point 107° after evaporation of the ether.

A larger quantity of the same substance may be obtained by nitration in sulphuric acid solution with the calculated quantity of $HNO_3$.

It has not yet been decided whether this compound is the still wanting nitro-sulpho-chloride, or possibly a dinitro-sulpho-chloride.

Added after the Dutch proof:

| | | |
|---|---|---|
| Calc.: | mononitro | N = 5.61 % |
| | dinitro | N = 9.64 % |
| Found: | | N = 5.62 % |

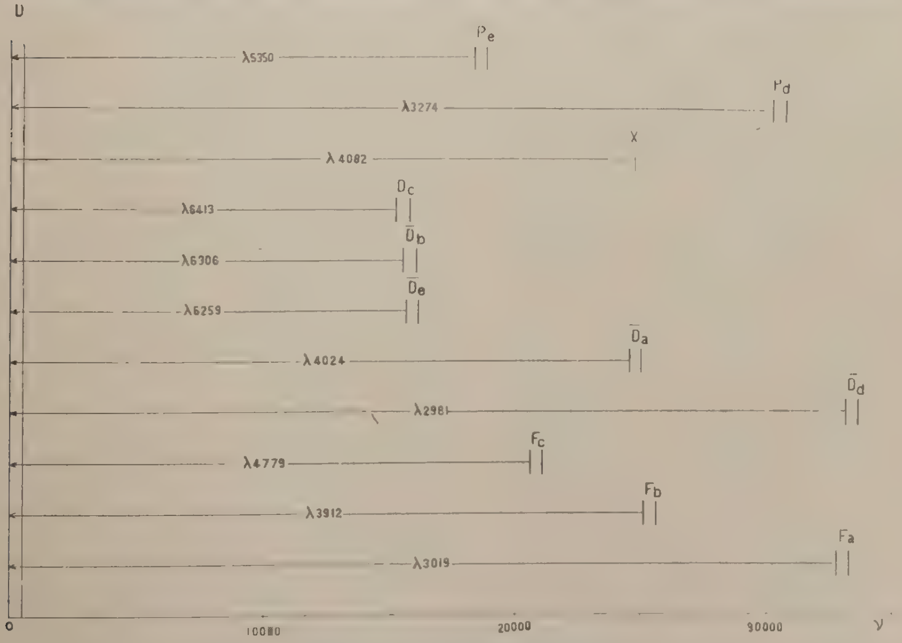
## **Physics.** — *"Magnetic Resolution of the Scandium Spectrum"*. (First Part).[1] By S. GOUDSMIT, J. VAN DER MARK, and Prof. P. ZEEMAN.

(Communicated at the meeting of December 27, 1924).

### *Classification of the lines.*

Several lines of the Scandium spectrum have been arranged into a term system by CATALÁN.[2] According to him the spectrum of neutral Scandium contains a doublet and a quartet term system, that of ionized Scandium a triplet system. The classification of CATALÁN, however, contains a few inaccuracies, which were evidently also perceived by GIESELER and GROTRIAN[3] in connection with their observations on the absorption in Scandium. From a theoretical point of view the rectification of the inaccuracies is important.

On account of the particular place which Scandium occupies in the periodic system of the elements — i.e. the first element in this system



Sc I Doubletsysteem.

Fig. 1.

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[1] Preliminary communications in Nature, Sept. 20, 1924, Naturw. 12, p. 743, 1924.

[2] M. A. CATALÁN. An. Soc. Esp. 20, p. 606, 1922, and 21, p. 464, 1923.

[3] H. GIESELER u. W. GROTRIAN. Zeitschr. f. Phys. 25, p. 342, 1924.

*Note added to the Dutch proof.* In the meantime a publication has appeared by CATALÁN with the corrected term system of ionized Scandium. An. Soc. Esp. 22, p. 497, 1924. Cf. also MEGGERS. Journal of the Washington Academy of Sciences, Vol. 14, N⁰. 18, Nov. 4. 1924.

## Sc I. DOUBLET SYSTEM.

| Doublet distance | Relative value of the term | Termsymbol | $J$ | $g$ |
|---|---|---|---|---|
| 168.5 | 0 | $D_2$ | 2 | 4/5 |
| | 168.5 | $D_1$ | 3 | 6/5 |
| 84.1 | 15672.4 | $\overline{D_2^c}$ | 2 | 4/5 |
| | 15756.5 | $\overline{D_1^c}$ | 3 | 6/5 |
| 0.8 | 16021.9 | $\overline{D_2^b}$ | 2 | 4/5 |
| | 16022.7 | $\overline{D_1^b}$ | 3 | 6/5 |
| 44.0 | 16096.9 | $\overline{D_2^e}$ | 2 | 4/5 |
| | 16140.9 | $\overline{D_1^e}$ | 3 | 6/5 |
| 144.6 | 18711.1 | $P_2^e$ | 1 | 2/3 |
| | 18855.7 | $P_1^e$ | 2 | 4/3 |
| 53.1 | 21032.8 | $F_2^c$ | 3 | 6/7 |
| | 21085.9 | $F_1^c$ | 4 | 8/7 |
| | 24656.7 | $X$ | — | — |
| 148.0 | 24866.1 | $\overline{D_2^a}$ | 2 | 4/5 |
| | 25014.1 | $\overline{D_1^a}$ | 3 | 6/5 |
| 140.1 | 25584.3 | $F_2^b$ | 3 | 6/7 |
| | 25624.4 | $F_1^b$ | 4 | 8/7 |
| 133.1 | 30573.7 | $P_2^d$ | 1 | 2/3 |
| | 30706.8 | $P_1^d$ | 2 | 4/3 |
| 124.4 | 33154.1 | $F_2^a$ | 3 | 6/7 |
| | 33278.5 | $F_1^a$ | 4 | 8/7 |
| 92.3 | 33614.8 | $\overline{D_2^d}$ | 2 | 4/5 |
| | 33707.1 | $\overline{D_1^d}$ | 3 | 6/5 |

in which completion of an internal group of electrons begins — it seemed of importance to us to confirm the classification of the lines through the examination of the magnetic resolutions, which is the chief end of this investigation.

ARRANGED LINES [1]). Sc I. DOUBLET SYSTEM.

| Arc intensity | λ. I. Å. | $\nu_{vac.}$ | Combination | Arc intensity | λ. I. Å. | $\nu_{vac.}$ | Combination |
|---|---|---|---|---|---|---|---|
| 2 | 2965.88 | 33707.0 | $D_2\ \overline{D_1^d}$ | 3 | 4753.16 | 21032.8 | $D_2\ F_1^c$ |
| 3 | 74.01 | 614.8 | $D_2\ \overline{D_2^d}$ | 3 | 79.41 | 20917.3 | $D_1\ F_1^c$ |
| 3 | 80.75 | 538.8 | $D_1\ \overline{D_2^d}$ | 1 | 91.56 | 864.2 | $D_1\ F_2^c$ |
| 2 | 89.00 | 446.3 | $D_1\ \overline{D_2^d}$ | 1 | 5301.97 | 18855.7 | $D_2\ P_1^e$ |
| 3 | 3015.34 | 33154.1 | $D_2\ F_2^a$ | 1 | 42.95 | 711.1 | $D_2\ P_2^e$ |
| 4 | 19.36 | 110.0 | $D_1\ F_1^a$ | 3 | 49.70 | 687.4 | $D_1\ P_1^e$ |
| 2 | 30.75 | 32985.6 | $D_1\ F_2^a$ | — | 6193.72 | 16140.9 | $D_2\ \overline{D_1^e}$ |
| 3 | 3255.67 | 30706.8 | $D_2\ P_1^d$ | 3 | 6210.68 | 096.9 | $D_2\ \overline{D_2^e}$ |
| 5 | 69.84 | 573.7 | $D_2\ P_2^d$ | 2 | 39.42 | 022.7 | $D_2\ \overline{D_1^b}$ |
| 5 | 73.65 | 538.2 | $D_1\ P_1^d$ | 2 | 39.78 | 021.8 | $D_2\ \overline{D_2^b}$ |
| 30 | 3907.54 | 25584.3 | $D_2\ F_2^b$ | 1 | 58.93 | 15972.8 | $D_1\ \overline{D_1^e}$ |
| 30 | 11.88 | 556.0 | $D_1\ F_1^b$ | 1 | 76.25 | 928.7 | $D_1\ \overline{D_2^e}$ |
| 6 | 33.44 | 415.9 | $D_1\ F_2^b$ | 10 | 6305.72 | 854.2 | $D_1\ \overline{D_1^b}$ |
| 15 | 3996.61 | 25014.1 | $D_2\ \overline{D_1^a}$ | — | 06.04 | 853.4 | $D_1\ \overline{D_2^b}$ |
| 20 | 4020.40 | 24866.2 | $D_2\ \overline{D_2^a}$ | 1 | 6344.82 | 15756.5 | $D_2\ \overline{D_1^c}$ |
| 30 | 23.68 | 845.9 | $D_1\ \overline{D_1^a}$ | 2 | 78.80 | 672.6 | $D_2\ \overline{D_2^c}$ |
| 10 | 47.81 | 697.8 | $D_1\ \overline{D_2^a}$ | 3 | 6413.32 | 588.2 | $D_1\ \overline{D_1^c}$ |
| 10 | 4054.56 | 24656.7 | $D_2\ X$ | — | 48.20 | 503.9 | $D_1\ \overline{D_2^c}$ |
| 15 | 82.44 | 488.3 | $D_1\ X$ | | | | |

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[1]) Wave-lengths and intensities according to EXNER and HASCHEK, corrected to I. Å.

## Sc II. TRIPLET SYSTEM.

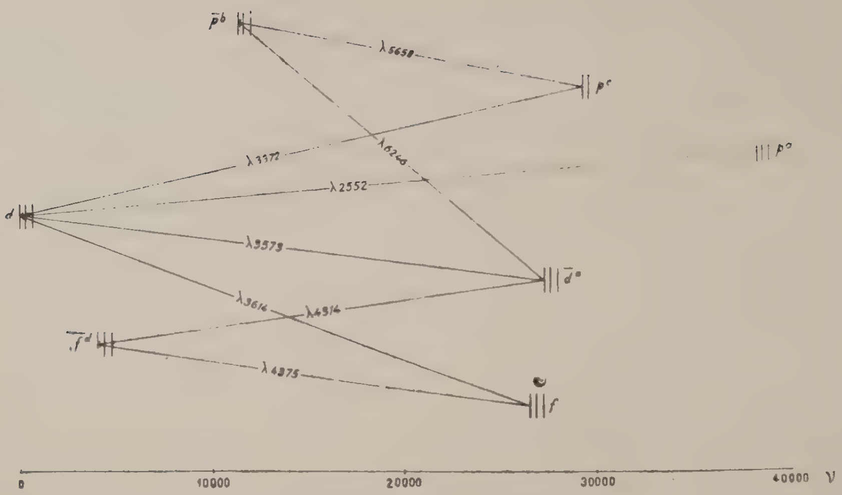
| Triplet distance | Relative value of the term | Termsymbol | $J$ | $g$ |
|---|---|---|---|---|
| | 0 | $d^3$ | $1^1/_2$ | $^1/_2$ |
| 67.6 | 67.6 | $d_2$ | $2^1/_2$ | $^7/_6$ |
| 110.2 | 177.8 | $d_1$ | $3^1/_2$ | $^4/_3$ |
| | 4802.4 | $\overline{f_3^d}$ | $2^1/_2$ | $^2/_3$ |
| 80.8 | 4883.2 | $\overline{f_2^d}$ | $3^1/_2$ | $^{13}/_{12}$ |
| 104.3 | 4987.5 | $\overline{f_1^d}$ | $4^1/_2$ | $^5/_4$ |
| | 12073.8 | $\overline{p_3^b}$ | $^1/_2$ | $^0/_0$ |
| 27.5 | 12101.3 | $\overline{p_2^b}$ | $1^1/_2$ | $^3/_2$ |
| 52.8 | 12154.1 | $\overline{p_1^b}$ | $2^1/_2$ | $^3/_2$ |
| | 27443.9 | $f_3$ | $2^1/_2$ | $^2/_3$ |
| 158.8 | 27602.7 | $f_2$ | $3^1/_2$ | $^{13}/_{12}$ |
| 238.7 | 27841.4 | $f_1$ | $4^1/_2$ | $^5/_4$ |
| | 27918.1 | $\overline{d_3^a}$ | $1^1/_2$ | $^1/_2$ |
| 103.5 | 28021.6 | $\overline{d_2^a}$ | $2^1/_2$ | $^7/_6$ |
| 139.4 | 28161.5 | $\overline{d_1^a}$ | $3^1/_2$ | $^4/_3$ |
| | 29742.3 | $p_2^c$ | $1^1/_2$ | — |
| 81.9 | 29824.2 | $p_1^c$ | $2^1/_2$ | $^3/_2$ |
| | 39002 | $p_3^a$ | $^1/_2$ | $^0/_0$ |
| 113 | 39115 | $p_2^a$ | $1^1/_2$ | $^3/_2$ |
| 231 | 39346 | $p_1^a$ | $2^1/_2$ | $^3/_2$ |

Here follows first of all the corrected term scheme for the doublet and the triplet system.

The term $d_3$, which was put equal to 0 here, very probably belongs

## ARRANGED LINES. Sc II. TRIPLET SYSTEM.

| Spark intensity | λ. I. Å. | $\nu_{vac.}$ | Combination | Spark intensity | λ. I. Å. | $\nu_{vac.}$ | Combination |
|---|---|---|---|---|---|---|---|
| — | 2540.86 | 39345.0 | $d_3\ p_1^a$ | 1 | 4279.93 | 23358.3 | $\overline{f_3^d}\ \overline{d_1^a}$ |
| 4 | 45.19 | 278.1 | $d_2\ p_1^a$ | 5 | 94.78 | 277.6 | $\overline{f_2^d}\ \overline{d_1^a}$ |
| 8 | 52.39 | 167.2 | $d_1\ p_1^a$ | 6 | 4305.72 | 218.4 | $\overline{f_3^d}\ \overline{d_2^a}$ |
| 4 | 55.82 | 114.6 | $d_3\ p_2^a$ | 30 | 14.09 | 173.4 | $\overline{f_1^d}\ \overline{d_1^a}$ |
| 6 | 60.28 | 046.5 | $d_2\ p_2^a$ | 20 | 20.75 | 137.7 | $\overline{f_2^d}\ \overline{d_2^a}$ |
| 4 | 63.21 | 002.0 | $d_3\ p_3^a$ | 20 | 24.99 | 115.0 | $\overline{f_3^d}\ \overline{d_3^a}$ |
| 2 | 3352.05 | 29824.5 | $d_3\ p_1^c$ | 5 | 4354.61 | 22957.7 | $\overline{f_2^d}\ f_1$ |
| 8 | 59.69 | 756.6 | $d_2\ p_1^c$ | 30 | 74.51 | 853.3 | $\overline{f_1^d}\ f_1$ |
| 8 | 61.31 | 742.3 | $d_3\ p_2^c$ | 5 | 84.80 | 799.7 | $\overline{f_3^d}\ f_2$ |
| 10 | 68.96 | 674.7 | $d_2\ p_2^c$ | 20 | 4400.39 | 718.9 | $\overline{f_2^d}\ f_2$ |
| 10 | 72.16 | 646.4 | $d_1\ p_1^c$ | 20 | 15.55 | 640.9 | $\overline{f_3^d}\ f_3$ |
| 20 | 3558.56 | 28093.3 | $d_2\ \overline{d_1^a}$ | 2 | 20.66 | 614.7 | $\overline{f_1^d}\ f_2$ |
| 20 | 67.72 | 021.1 | $d_3\ \overline{d_2^a}$ | 3 | 31.36 | 560.1 | $\overline{f_2^d}\ f_3$ |
| 50 | 72.57 | 27983.1 | $d_1\ \overline{d_1^a}$ | 1 | 5641.00 | 17722.5 | $\overline{p_2^b}\ p_1^c$ |
| 30 | 76.37 | 953.3 | $d_2\ \overline{d_2^a}$ | 2 | 57.89 | 669.5 | $\overline{p_1^b}\ p_1^c$ |
| 20 | 80.98 | 917.4 | $d_3\ \overline{d_3^a}$ | 1 | 58.35 | 668.1 | $\overline{p_3^b}\ p_2^c$ |
| 10 | 89.67 | 849.8 | $d_2\ \overline{d_3^a}$ | 1 | 67.19 | 640.5 | $\overline{p_2^b}\ p_2^c$ |
| 10 | 90.52 | 843.2 | $d_1\ \overline{d_2^a}$ | 1 | 84.22 | 587.7 | $\overline{p_1^b}\ p_2^c$ |
| 100 | 3613.83 | 27663.6 | $d_1\ f_1$ | 1 | 6245.64 | 16006.8 | $\overline{p_1^b}\ \overline{d_1^a}$ |
| 100 | 30.75 | 534.7 | $d_2\ f_2$ | 1 | 79.74 | 15919.8 | $\overline{p_2^b}\ \overline{d_2^a}$ |
| 50 | 42.96 | 443.6 | $d_3\ f_3$ | — | 6300.64 | 867.0 | $\overline{p_1^b}\ \overline{d_2^a}$ |
| 15 | 45.48 | 424.6 | $d_1\ f_2$ | 1 | 09.94 | 843.6 | $\overline{p_3^b}\ \overline{d_3^a}$ |
| 20 | 51.99 | 375.7 | $d_2\ f_3$ | — | 20.85 | 816.3 | $\overline{p_2^b}\ \overline{d_3^a}$ |
| 3 | 66.68 | 266.0 | $d_1\ f_3$ | — | 42.02 | 763.5 | $\overline{p_1^b}\ \overline{a_3^a}$ |



ScII Tripletsysteem.

Fig. 2.

to the lowest of the levels of energy discussed here. Whether it is also the lowest possible level of ionized Scandium cannot be decided as yet.

*Experimental part.*

In the investigation a concave Rowland grating was used as spectrograph, mounted in the way indicated by EAGLE [1]). The grating has 14438 lines to the inch; width 5 inches (originally 6 inches), a strip of 1 inch on one of the sides of the grating gave rise to disturbances, and was therefore covered when the photo was taken; radius of curvature 21 feet.

The photos were taken in the 2nd order on plates 50 cm. long, which covered an area of about 600 Å, so that the dispersion amounted to about 1,2 Å per mm. The drawback of the EAGLE mounting is that the photographic focussing must be made anew for every area. As source of light a MERTON vacuum iron arc lamp appeared to be very efficient [2]). With the ordinary iron arc in air the very delicate adjustment necessary for the photographing of the resolution figures, was much more difficult to attain on account of the lines being less fine.

The brightness of the grating is rather small, so that exposures of 5 hours appeared to be necessary.

The magnetic field was produced by a Weiss-magnet with water cooling which gave a field of about 41000 Gauss with the distance of the poles used and with a current of 100 Ampères. The current was supplied by a converter, with which the strength of the current could be kept sufficiently constant. The cooling of the magnet was very efficient, so much so that its temperature was lower than that of the room.

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[1]) Astroph. Journ. 31, p. 120, 1910.

[2]) Prof. MERTON was so kind as to put a drawing of his lamp at the disposal of one of us (P. Z.).

As source of light in the field a vacuum trembler was used, a modification of BACK'S Abreissbogen [1]). The modification consists in this that the mechanical arrangement that works the tungsten electrode in BACK'S experiment, has been discarded, and that the current itself works it. The arrangement is briefly this [2]): the tungsten electrode is fastened to a pendulum, which can move freely in the direction from pole to pole. By means of a feeble spring with a tension adjustable from the outside, the tungsten electrode is always pressed against the other, fixed electrode.

The whole apparatus is made so small that it can be contained inside the vacuum pot which is placed between the pole pieces, and fastened, like the other electrode, to a ground-in metal stopper, so as to render quick removal possible. Now the current must pass through a solenoid which is fastened to the pendulum, and the axis of which is at right angles to the direction of the lines of force between the polar pieces of the magnet. The solenoid is still in a very strong field, so that it need have only few turns to draw the tungsten electrode from the other and produce an interrupting spark or arc, if the current direction be chosen well.

The spark burned in hydrogen of low pressure, just as in BACK'S arrangement. We, however, admitted hydrogen through a narrow capillary, which was sucked off again by a slowly running Gaede pump, so that we experienced less trouble of small leakages, which are sometimes inevitable.

Scandium being unknown in metallic state, it was not possible to use a metal electrode for the spark. We were, therefore, obliged to have recourse to carbon electrodes. Carbon pieces, sawn out of arc-lamp carbon, appeared too much liable to breakage, on account of the required small dimensions (about 20 × 1 × 1.5 mm.), and they contained too many contaminations. This induced us to make the carbon pieces ourselves. The material for them is soot, obtained from a smoking kerosene flame. This is mixed with anhydrous coal tar, kneaded, and at last beaten till a very stiff paste is obtained. By the aid of a very simple compressing cylinder with piston placed in a bench vice, this paste is spouted to a long thread with the required rectangular cross-section. This thread is cut to pieces of the desired length. The carbon pieces, which are still soft, are carefully packed in a crucible with graphite, and kept yellow-red hot for three quarters of an hour. After the outer crust of graphite had been ground off, strong metallic-sounding carbon pieces were obtained, which hardly ever broke.

Carbons, into which Scandium oxide had already been entered during the preparation, appeared to give only a feeble spectrum. Carbon soaked in the chloride, appeared to give a better result. In order to introduce as much Scandium into the carbons as possible, the carbons were first kept under vacuum for a long time, then a concentrated Scandium solution was admitted, after which the vacuum was broken. The carbons obtained in this way, contained only very weak contaminations, chiefly calcium.

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[1]) Ann. d. Phys. Bd. 70, 1923, p. 336.

[2]) A more detailed description will follow.

The application of carbons in the vacuum trembler has a drawback, viz. that the tungsten electrode is pretty quickly consumed. This is the reason that we do not apply as BACK a ground tungsten electrode of a definite shape, but an ordinary tungsten filament (thickness 0,6 mm.) which can be easily replaced. The carbons themselves are only very slowly consumed, one carbon is sufficient for four hours' illumination.

The plates have been measured in four different ways;

1. with the comparator,
2. with the micro-photometer,
3. in the projected image.

For sharp lines of a certain degree of blackness the comparator appeared the most suitable method, the micro-photometer gave the best results for diffuse lines (pseudo-triplets and similar lines), the last method appearing to be the best for exceedingly weak lines. An image of the lines was thrown on a screen with a known magnification by micro-projection, and then measured. Very feeble lines for which the adjustment could not be made accurately in the comparator, and which could not be seen in consequence of the grain in the micro-photogram, could still be measured very well by this method. In the measurement of very diffuse lines the adjustment was made for the centre of gravity of the blackening; for some of these lines it was also still possible to make the adjustment for the sharp boundary line of the components, which measurement was then in good agreement with theory.

Measurements were made in the regions of 3900—4500 Å, and 3200—3900 Å. Other regions will follow. At the moment a new, much brighter grating arrangement is being constructed in the laboratory, which will be taken in use very soon. With this apparatus some other parts of the spectrum wil be examined, besides other lines, which are still doubtful. Between 3900—4500 Å the normal triplet distance has been calculated from the resolutions of the calcium triplet $\lambda$ 4226 and the calcium quadruplet $\lambda$ 3968. The calcium sextet $\lambda$ 3933 also occurs on the photographic plates; at some tenths of Å there occurs a very feeble Scandium line, which all the same deforms the sextet perceptibly.

Starting from the region of 3200 Å there did not occur a single foreign line suitable for a determination of the intensity of the field. From the photographs in the preceding region it had, however, already been ascertained, what resolutions the Scandium lines $\lambda\lambda$ 3572, 3576, and 3581 would have to present. These lines give all three sharp triplets. We have used these lines for the determination of the intensity of the field. This appears to be justified on account of the good agreement presented by the resolutions of the other Scandium lines with the resolutions predicted.

We have, therefore, omitted to take a special photograph for the determination of the field intensity.

On the whole the Scandium lines, even the sharp triplets, are somewhat diffuse. Consequently the attainable accuracy is not very great. It is, of course, also different for different lines. As a general datum for the accuracy of the measurements it may be stated that the position of the components could be determined up to an average of 0,006 Å. For sharp lines the mean deviation from the mean value was 0,0025 mm. = 0,0033 Å for a series of 10 observations, it increased to 0,008 mm. = 0,010 Å for very hazy lines. When it is also stated that the widest resolution was ± 0,66 Å from central to outer component, and the narrowest ± 0,12 Å, it appears that the error which will be finally present in the result, can never be very small.

## THE MAGNETIC RESOLUTIONS.

### *Sc I Doublet system.*

Combinations *DD*

$\lambda$ **3996.61** $D_2\overline{D}{}^a_1$ $J=2,\ g=\frac{4}{5}$ with $J=3,\ g={}^6/_5$

type $\frac{(1\ 3)\ 57\ \mathbf{9}}{5}$

observed **1.79** 1.40 1.00 (0.62) (**0.19**) (**0.19**) (0.56) 0.98 1.40 **1.76**

calculated **1.80** 1.40 1.00 (0.60) (**0.20**) (**0.20**) (0.60) 1.00 1.40 **1.80**

$\lambda$ **4020.40** $D_2\overline{D}{}^a_2$ $J=2,\ g=\frac{4}{5}$ with $J=3,\ g=\frac{4}{5}$

type $\frac{(0)\ 4}{5}$

observed 0.80 (0) 0.81 sharp

calculated 0.80 (0) 0.80 sharp

$\lambda$ **4023.68** $D_1\overline{D}{}^a_1$ $J=3,\ g=\frac{6}{5}$ with $J=3,\ g={}^6/_5$

type $\frac{(0)\ 6}{5}$ Fig. 3

observed 1.21 (0) 1.21 sharp

calculated 1.20 (0) 1.20 sharp

$\lambda$ **4047.81** $D_1\overline{D}{}^a_2$ $J=3,\ g={}^6/_5$ with $J=2,\ g={}^4/_5$

type $\frac{(1\,3)\,5\,7\,\mathbf{9}}{5}$

observed **1.77** 1.39 0.98 (0.59) (**0.19**) (**0.19**) (0.56) 0.96 1.33 **1.71**

calculated **1.80** 1.40 1.00 (0.60) (**0.20**) (**0.20**) (0.60) 1.00 1.40 **1.80**

The observed resolution of this group fully agrees with the calculations.

This confirms, therefore, that we have really to do here with a doublet *DD*-group. The asymmetries are real.

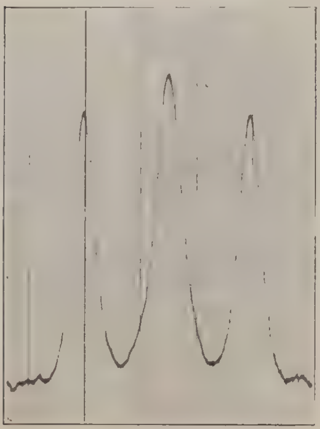

Fig. 3. λ 4023.68.

Accordingly these resolutions also confirm GIESELER and GROTRIAN's ¹) view that the fundamental term of *Sc I* is a doublet *D*-term; for according to their absorption experiments it is the term $D_2$ put equal to 0 in our term system.

According to BOHR and COSTER ²) the neutral Scandium atom must contain one $3_3$- and two $4_1$-electrons. If during the emission this $3_3$-electron were still present in the atom rest, so-called terms "höherer Stufe" with entirely new resolutions would have to be expected according to LANDÉ ³). As this is very certainly not the case, their $3_3$-electron must necessarily be the emitting electron. This is also in harmony with STONER's ⁴) electron system, according to which the fundamental term must then have the symbol $3_{32}$. For the fundamental path $J$ is actually $= 2$.

Except under special circumstances the splitting up of the group furnishes already an important support for the accuracy of the other term symbols. For from the way in which the other terms combine with the known *D*-fundamental term, it is possible to determine their quanta-values $J$, hence to establish the term symbol with pretty great certainty.

Further the following lines were split up:

**λ 3907.54** $D_2 F_2^b$ $\qquad J=2,\ g={}^4/_5$ with $J=3,\ g={}^6/_7$

type $\dfrac{(1\ 3)\quad 27\ 29\ 31\ 33}{35}$

| | | | | |
|---|---|---|---|---|
| observed | 0.90 | (0) | 0.91 | pretty sharp |
| calculated | $<$ 0.94 | (0) $<$ | 0.94 | pretty sharp |

**λ 3911.88** $D_1 F_1^b$ $\qquad J=3,\ g={}^6/_5$ with $J=4,\ g={}^8/_7$

type $\dfrac{(1\ 35)\quad 35\ 37\ 39\ 41\ 43\ 45}{35}$

| | | | | |
|---|---|---|---|---|
| observed | 1.07 | (0) | 1.06 | sharp inside |
| calculated | $>$ 1.00 | (0) $>$ | 1.00 | sharp inside |

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¹) loc. cit.

²) N. BOHR and D. COSTER, Zeitschr. f. Phys. 12, p. 342, 1923.

³) A. LANDÉ, Zeitschr. f. Phys., 17, p. 292, 1923.

⁴) E. C. STONER, Phil. Mag. 48, 719, 1924.

λ **3269.84** $D_2 P_2^d$ $J=2\ g={}^4/_5$ with $J=1,\ g={}^2/_3$

type $\frac{(1)\ 11\ \mathbf{13}}{15}$

observed 0.87 (0) 0.76 feeble, vague
calculated 0.86 0.74 (0.07) (0.07) 0.74 0.86

*Sc II Triplet system.*

Combinations *dd*

λ **3558.56** $d_2 \overline{d}{}_1^a$ $J=2\frac{1}{2}\ g={}^7/_6$ with $J=3\frac{1}{2},\ g={}^4/_3$

type $\frac{(\mathbf{0}\ 1\ 2)\ 6\ 7\ 8\ 9\ \mathbf{10}}{6}$

observed 1.63 (0) 1.64 sharp outside
calculated $<$ 1.67 (0) $<$ 1.67 sharp outside

λ **3567.72** $d_3 \overline{d}{}_2^a$ $J=1\frac{1}{2},\ g={}^1/_2$, with $J=2\frac{1}{2},\ g={}^7/_6$

type $\frac{(\mathbf{0})\ 3\ (4)\ 7\ \mathbf{11}}{6}$

observed **1.83** 1.16 0.64 **(0)** 0.64 1.15 **1.82**
calculated **1.83** 1.17 $\overbrace{(0.67)\ 0.50}$ **(0)** $\overbrace{0.50\ (0.67)}$ 1.17 **1.83**

The measurement was made on a plate on which the two polarisation states had been photographed at the same time. In consequence of this the stronger $\pi$ component (0.67) had combined with the weak $\sigma$ component 0.50. Fig. 4.

λ **3572.57** $d_1 \overline{d}{}_1^a$ $J=3\frac{1}{2},\ g={}^4/_3$ with $J=3^1/_2,\ g={}^4/_3$

type $\frac{(0)\ 4}{3}$

observed 1.31 (0) 1.34 sharp
calculated 1.33 (0) 1.33 sharp

λ **3576.37** $d_2 \overline{d}{}_2^a$ $J=2\frac{1}{2},\ g={}^7/_6$ with $J=2\frac{1}{2},\ g={}^7/_6$

type $\frac{(0)\ 7}{6}$

observed 1.14 (0) 1.19 sharp
calculated 1.17 (0) 1.17 sharp

λ **3580.98** $d_3 \overline{d}{}_3^a$ $J=1\frac{1}{2},\ g=1\frac{1}{2}$ with $J=1\frac{1}{2},\ g=\frac{1}{2}$

type $\frac{(0)\ 1}{2}$

observed 0.51 (0) 0.51 sharp
calculated 0.50 (0) 0.50 sharp

λ **3589.67** $d_2 \overline{d}{}_3^a$ $J=2\frac{1}{2},\ g={}^7/_6$ with $J=1\frac{1}{2},\ g={}^1/_2$

type $\frac{(\mathbf{0})\ 3\ (4)\ 7\ \mathbf{11}}{6}$

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| observed | **1.83** | 1.17 | 0.65 | | **(0)** | 0.61 | | 1.18 | [**1.76**] |
| calculated | **1.83** | 1.17 | (0.67) | 0.50 | (0) | 0.50 | (0.67) | 1.17 | **1.83** |

Compare remark to λ 3567.72. The component [1.76] coincides with the component [1.42] of the following line. Fig. 5.

λ **3590.52** $d_1 \overline{d}_2^{a}$ $J = 3\frac{1}{2}$, $g = {}^4/_3$ with $J = 2\frac{1}{2}$, $g = {}^7/_6$

$$\text{type } \frac{(\mathbf{0}\ 1\ 2)\ 6\ 7\ 8\ 9\ \mathbf{10}}{6}$$

| | | | | |
|---|---|---|---|---|
| observed | [1.42] | (0) | 1.51 | sharp outside |
| calculated | < 1.67 | (0) | < 1.67 | sharp outside |

Splitting up too simple, comp. λ 3558.56.

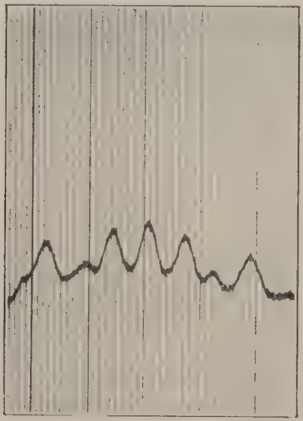

Fig. 4. λ 3567.62

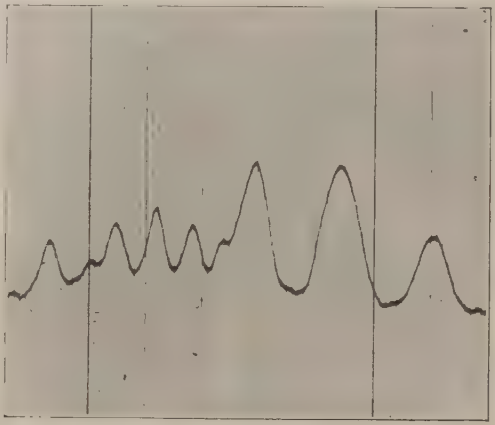

Fig. 5. λ 3589.67 and λ 3590.72.

## Combinations *df*.

λ **3613.83** $d_1 f_1$ $J = 3\frac{1}{2}$, $g = {}^4/_3$ with $J = 4\frac{1}{2}$, $g = {}^5/_4$

$$\text{type } \frac{(\mathbf{0}\ 1\ 2\ 3)\ \mathbf{12}\ 13\ 14\ 15\ 16\ 17\ 18}{12}$$

| | | | | |
|---|---|---|---|---|
| observed | 1.11 | (0) | 1.12 | sharp inside |
| calculated | > 1.00 | (0) | > 1.00 | sharp inside |

λ **3630.75** $d_2 f_2$ $J = 2\frac{1}{2}$, $g = {}^7/_6$ with $J = 3\frac{1}{2}$, $g = {}^{13}/_{12}$

$$\text{type } \frac{(\mathbf{0}\ 1 2\ 3)\ \mathbf{11}\ 12\ 13\ 14\ 15\ 16}{12}$$

| | | | | |
|---|---|---|---|---|
| observed | 1.03 | (0) | 1.03 | sharp inside |
| calculated | > 0.92 | (0) | > 0.92 | sharp inside |

Splitting up too great comp. λ 4320.75.

λ **3642.96** $d_3 f_3$ $J = 1\frac{1}{2}$, $g = {}^1/_2$ with $J = 2\frac{1}{2}$, $g = {}^2/_3$

$$\text{type } \frac{(\mathbf{0}\ 1)\ 3\ 4\ \mathbf{5}}{6}$$

| | | | | |
|---|---|---|---|---|
| observed | 0.78 | (0) | 0.79 | very broad |
| calculated | < 0.83 | (0) | < 0.83 | sharp outside |

$\lambda$ **3645.48** $d_1 f_2$ $J = 3\frac{1}{2},\ g = {}^{4}/_{3}$ with $J = 3\frac{1}{2},\ g = {}^{13}/_{12}$

type $\frac{(3\ 6\ 9)\ \ 7\ 10\ \mathbf{13}\ \mathbf{16}\ 19\ 22}{12}$

| | | | | | |
|---|---|---|---|---|---|
| observed | ? | 0.69 | 0.68 | ? | ⊥ very vague |
| calculated | 1.21 | $<$(0.75) | $<$(0.75) | 1.21 | ⊥ not sharp |

$\lambda$ **3651.99** $d_2 f_3$ $J = 2\frac{1}{2},\ g = {}^{7}/_{6}$ with $J = 2\frac{1}{2},\ g = {}^{2}/_{3}$

type $\frac{1\ (3)\ \ \mathbf{4}\ (6)\ \mathbf{7}\ 10}{6}$

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| observed | 1.58 | 1.00 | 0.57 | | | 0.57 | 1.04 | 1.67 |
| calculated | 1.67 | $\overbrace{\mathbf{1.17}\ (\mathbf{1.00})}$ | $\overbrace{\mathbf{0.67}\ (0.50)}$ | 0.16 | 0.16 | $\overbrace{(0.50)\ \mathbf{0.67}}$ | $\overbrace{(\mathbf{1.00})\ \mathbf{1.17}}$ | 1.67 |

Cf. remark to $\lambda$ 3567.72. Asymmetric, inner components too weak.

$\lambda$ **4314.09** $\overline{f}{}^{d}_{1}\,\overline{d}{}^{a}_{1}$ $J = 4\frac{1}{2},\ g = {}^{5}/_{4}$ with $J = 3\frac{1}{2},\ g = {}^{4}/_{3}$

type $\frac{(\mathbf{0}\ 1\ 2\ 3)\ \ \mathbf{12}\ 13\ 14\ 15\ 16\ 17\ 18}{12}$

| | | | | |
|---|---|---|---|---|
| observed | 1.09 | (0) | 1.10 | sharp inside |
| calculated | $>$1.00 | (0) | $>$1.00 | sharp inside |

$\lambda$ **4320.75** $\overline{f}{}^{d}_{1}\,\overline{d}{}^{a}_{2}$ $J = 3\frac{1}{2},\ g = {}^{13}/_{12}$ with $J = 2\frac{1}{2},\ g = {}^{7}/_{6}$

type $\frac{(\mathbf{0}\ 1\ 2\ 3)\ \ \mathbf{11}\ 12\ 13\ 14\ 15\ 16}{12}$

| | | | | |
|---|---|---|---|---|
| observed | 0.98 | (0) | 0.96 | sharp inside |
| calculated | $>$0.92 | (0) | $>$0.92 | sharp inside |

$\lambda$ **4325.00** $\overline{f}{}^{d}_{3}\,\overline{d}{}^{a}_{3}$ $J = 2\frac{1}{2},\ g = {}^{2}/_{3}$ with $J = 1\frac{1}{2},\ g = {}^{1}/_{2}$

type $\frac{(\mathbf{0}\ 1)\ \ 3\ 4\ \mathbf{5}}{6}$

| | | | | |
|---|---|---|---|---|
| observed | 0.79 | (0) | 0.79 | sharp outside |
| calculated | $<$0.83 | (0) | $<$0.83 | sharp outside |

Combinations *ff*.

$\lambda$ **4374.51** $\overline{f}{}^{d}_{1}\,f_1$ $J = 4\frac{1}{2},\ g = {}^{5}/_{4}$ with $J = 4\frac{1}{2},\ g = {}^{5}/_{4}$

type $\frac{(0)\ \ 5}{4}$

| | | | | |
|---|---|---|---|---|
| observed | 1.28 | (0) | 1.37 | sharp |
| calculated | 1.25 | (0) | 1.25 | sharp |

$\lambda$ **4400.39** $\overline{f}{}^{d}_{2}\,f_2$ $J = 3\frac{1}{2},\ g = {}^{13}/_{12}$ with $J = 3\frac{1}{2},\ g = {}^{13}/_{12}$

type $\frac{(0)\ \ 13}{12}$

| | | | | |
|---|---|---|---|---|
| observed | 1.09 | (0) | 1.10 | sharp |
| calculated | 1.08 | (0) | 1.08 | sharp |

λ **4415.55** $\bar{f}_1^{d} f_1$ $J = 2\frac{1}{2},\ g = {}^2/_3$ with $J = 2\frac{1}{2},\ g = {}^2/_3$

type $\frac{(0)\ 2}{3}$

observed 0.69 (0) 0.67 sharp

calculated 0.67 (0) 0.67 sharp

Combinations *dp*.

λ **3372.16** $d_1\, p_1^c$ $J = 3\frac{1}{2},\ g = {}^4/_3$ with $J = 2\frac{1}{2},\ g = {}^3/_2$

type $\frac{(\mathbf{0}\ 12)\ \mathbf{6}\ 7\ 8\ 9\ 10}{6}$

observed 1.16 (0) 1.13 sharp inside

calculated $> 1.00$ $(0) > 1.00$ sharp inside

λ **3359,69** $d_2\, p_1^c$ $J = 2\frac{1}{2},\ g = {}^7/_6$ with $J = 2\frac{1}{2},\ g = {}^3/_2$

type $\frac{(2\ \mathbf{4})\ 5\ \mathbf{7}\ \mathbf{9}\ 11}{6}$

observed ? 0.66 0.66 ? very vague

calculated $1.33 < (0.67) < (0.67)$ 1.33 ⊥ broad, not sharp

Unclassified lines.

λ **3353,74**

observed 1.00 (0) 1.00 not sharp

λ **3535,74**

observed 0.98 (0) 1.02 sharp

λ **4246,88**

observed 0.99 (0) 0.98 pretty sharp

Accordingly these lines, which give normal triplets, probably belong to the simple term system of ionized Scandium.

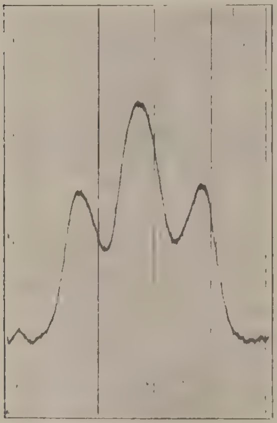

Fig. 6. λ 4325.00.

It may be pointed out here that splitting-up types, which in *sp*-combinations are still easily resoluble, can no longer be resolved in *dd*-, *df*- and other combinations, as also the original lines are generally much less sharp.

The investigation of some important lines is still in progress. These are first of all the *ScI*-lines λ 4054.56 and λ 4082.44. The intensity of these lines greatly decreases in the magnetic field, so that it was not yet possible to measure out the resolutions. Preliminary observations render it, however, probable that the effect met with here is the partial Paschen-Back effect, so that the term denoted by $X$ in the term system is probably a doublet $P$, $D$ or $F$ term that has coincided.

More or less the same thing seems to be the case with the triplet term $p^c$. Probably *two* terms of this, $p_2^c$ and $p_3^c$, seem to have almost coincided. The fuller examination of the resolution of the lines λ 3368 and λ 3361 must still confirm this.

The correctness of the classification of the lines of ionized Scandium appears from the resolutions given above. So far no terms "höherer Stufe" were found in this either. We may, therefore, refer to the recently analyzed spectrum of the allied ionized Lanthanum ¹). From earlier measurements of the magnetic resolution ²) it appeared with certainty that there occur a number of these terms "höherer Stufe" in this spectrum. Possibly these are found only in feeble lines in the Scandium spectrum.

In conclusion we may express our cordial thanks to Messrs. Prof. BOHUSLAV BRAUNER, and Prof. ŠTĚRRA—BÖHM at Prague, who enabled us to carry out this investigation, by supplying us with perfectly pure $Sc_2O_3$.

*Amsterdam*, December 1924. *Laboratory "Physica"*.

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¹) S. GOUDSMIT, These Proceedings 28 p. 23, Naturw. 12, p. 851, 1924.

²) S. RYBAR, Phys. Zeitschr. 12, p. 889, 1911.

## **Astronomy.** — *"The Light-Curve of the Cepheids"*. By Prof. A. A. NIJLAND.

(Communicated at the meeting of January 31, 1925).

It has been tried to establish a connection between the Cepheids and the semi-regular long-period variable stars of the Mira-type. In fact, in some respects the mean curve of the Cepheids may be considered as a reduced copy of that of the long-period variables, assuming for a moment, that there can be question of mean curves for phenomena each presenting so much variety. If for the mean periods of Cepheids and long-period variables $6^d$ and $300^d$ is taken, respectively, a proportion of 50 is found, which presents itself also in the range of the light variation, at least when magnitudes are converted into light-intensities. For the ratio 50 corresponds to a difference of $4^1/_4$ magnitudes; and, as a matter of fact, this is about what observation has taught about the difference of range of the mean light-variation of Cepheids ($1^m$) and long-period variables ($5^m$). It is to be remarked, however, that the light-intensity curve of the Mira-variables resembles more closely that of e.g. $V\,18 = RZ$ *Camelopardalis* or $V\,18 = RZ$ *Lyrae* [1]) than that of $\delta$ *Cephei.*

It is interesting to ascertain whether the asserted analogy goes still further. The semi-regular variables of the Mira-type exhibit irregularities both in period and in amplitude. Moreover the light-curves have every now and then secondary undulations or humps, which often attain a full magnitude, and can be proved to exist beyond any doubt. No unanimity has been reached on the question whether this is the case in the same degree also with the Cepheids. It will be readily admitted that without doubt all these irregularities will occur here too *occasionally*. The secondary wave with *S Sagittae* is incontestable, and the case of $\eta$ *Aquilae* [2]), which is perfectly confirmed by simultaneous Utrecht observations [3]), speaks for itself. Whether, however, the changes, which according to some astronomers are supposed to continually modify the light-curve of e.g. $V\,49 = XX$ *Cygni* [4]), are all real, may be questioned; and likewise whether this is the case with the numerous secondary inflexions, which many authors draw in the light-curves of the Cepheids observed by them.

I propose to discuss the question whether *as a rule* the light-curves of the Cepheids can be drawn smooth and tense, and whether the period and the extent of the light-variation may *as a rule* be considered so nearly constant that a mean light-curve may be constructed. The question is of importance also for this reason that in the pulsation theory, which is founded on a physical base, secondary undulations are more readily accepted than in the purely geometrical double star theory. It may, however, be pointed out that also in the latter there is every reason to assume physical disturbances of the smooth geometric process, since the spectrum is known to change [5]).

It seemed of importance to discuss the errors occurring in my Cepheid curves, and to compare them with the errors of the Algol variable curves, which for obvious reasons must be drawn smooth and tense.

Too often the term secondary wave is erroneously applied to what is simply an effect of errors of observation; the astronomical literature presents numerous examples of this misunderstanding. In my opinion, this is due to two different causes.

First of all a light-curve is often founded on too few observations. LAU [6]) derives a light-curve of $\eta$ Aquilae from only 56 estimates; the existence of a deep secondary wave appears to be dependent on the reliability of *two* successive observations, both giving a smaller brightness than corresponds with a smooth curve. KIESS [7]) derives a curve of $V\,12 = RT$ *Aurigae* from 66 photometric observations, and assumes in it no less than 3 secondary undulations of a depth of $0^m.1$, which cannot but make a somewhat arbitrary impression; the curve would present a totally different aspect when a different grouping to normal places had been chosen. About this point and in general about the way in which the observations have been reduced, KIESS leaves us in the dark. At all events it seems impossible, that these not over-accurate observations (the mean error is $0^m.13$) could say anything with certainty about undulations of $0^m.1$.

In the second place the curve traced follows the observations *too closely*; the amount of the inevitable errors of observation is accordingly not sufficiently taken into account. A striking example is furnished by SPERRA [8]), whose curve of $V\,23 = SW$ *Draconis* follows the normal places, as if there were no errors of observation at all. In the same number of the Astronomische Nachrichten ICHINOHE publishes a curve of $V\,26 = SZ$ *Aquilae*, in the descending branch of which he assumes a hump; if, however, the curve is drawn smooth, the deviations are no greater, nay, even smaller than ICHINOHE himself allows in the neighbourhood of the minimum. LEINER speaks of a "scharf ausgeprägte sekundäre Welle" in the light-curve of $V\,42 = VX$ *Cygni*, while a glance at the plotted normal places leads to the conviction that there is at least as much room for some other inflexions not assumed by LEINER, and that a smooth curve leaves deviations, which are perfectly admissible.

It is self-evident that the mean error must decide the question in every particular case, but, strange enough, this is often not given by the authors, so that any possibility of control is wanting.

In order to arrive at an impartial judgment, four conditions should in my opinion be observed as accurately as possible:

1. The algebraic sum of the deviations $\delta$ (normal point minus curve) should be 0;

2. an equal number of plus and minus signs should be found in the series of deviations, and likewise

3. an equal number of permanences of sign and of variations;

4. the mean error $\varepsilon_0$ derived *a posteriori* from the deviations $\delta$ should not be much greater than the m. e. $\varepsilon_1$, which is to be expected *a priori* on account of the internal agreement of the normal places, and which follows from the m. e. $\varepsilon$ of one observation through division by $\sqrt{m}$ (where $m$ is the number of observations of a normal place).

If on these conditions a tense curve can be drawn, it is improbable that real significance should be assigned to the secondary waves, and it is preferable to leave them alone for the present, and direct one's full attention to the main problem.

Probably — but unfortunately this cannot be verified — $\varepsilon_0$ is considerably *smaller* than $\varepsilon_1$ in the cases cited above, and this would be irreconcilable with the circumstance, that in the derivation of $\varepsilon_0$ always new systematic errors occur, so that necessarily $\varepsilon_0$ must be found greater than $\varepsilon_1$.

In a total of 19 light-curves (17 Cepheids)[10]) I met with only two cases (*S Sagittae* and *η Aquilae*), where secondary waves could not be dispensed with. The table shows in how far the above-mentioned conditions are satisfied. For a comparison the results of a discussion of 36 Algol-stars *) have been added (see further on).

| | Cepheids | Algol-stars |
|---|---|---|
| m. e. $\varepsilon$ of an observation | $0^m.104$ | $0^m.125$ |
| m. e. $\varepsilon_1$ of a normal place | 0.029 | 0.036 |
| m. e. $\varepsilon_0$ (normal place minus curve) | 0.031 | 0.046 |
| number of plus signs | 135 | 353 |
| „ noughts | 86 | 124 |
| „ minus signs | 129 | 363 |
| „ permanences | 111 | 373 |
| „ variations | 153 | 343 |

Two remarks about the Cepheids should be made here. First of all $\varepsilon_0$ appears to be about equal to $\varepsilon_1$, though in consequence of the appearance of new systematic errors it might be expected that $\varepsilon_0$ would come out considerably greater. It should further be noted that the number of permanences is much smaller than the number of variations. It follows from both remarks that, though only twice a secondary wave was assumed, yet in general the curves followed the normal points still too closely, and should have been drawn still tenser. The smoothing down of the curves gives rise to permanences, since the inflexions, that are removed, are based on at least two normal places: indeed, if an inflexion should be founded on only one normal place, it will not be accepted as real, for fear of falling into the error committed by LAU.

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*) Besides these 36 there are still ten ready for publication, but it will not be easy to find the necessary funds to publish this bulky material *in originali*.

This is in my opinion the cause of the secondary waves which many observers, erroneously as it seems to me, assume to be a real phenomenon in their light-curves, whereas they should simply be taken as permanences of sign, which must necessarily occur according to the laws of chance, even when the phenomenon under examination should have to be represented by a perfectly smooth curve: every curve based on observations must exhibit secondary waves, even though the phenomenon observed does not in any way give rise to them.

By way of check it seemed interesting to examine the available Algol-stars with respect to the errors of their light-curves, since these must certainly be drawn tense. These stars have been observed in exactly the same way, with the same instruments and by the same observer as the Cepheids. The results are placed side by side with those of the Cepheids. That the number of permanences is equal to that of the variations suggests a normal distribution of errors.

For the Algol-stars the great value of the mean errors should be noted.

*a*. First of all the m.e. $\varepsilon$ of one observation (hence also the m.e. $\varepsilon_1$ of a normal place, generally formed from 12 observations) is considerably greater with the Algol-stars than with the Cepheids. I am inclined to attribute this to a greater influence of the systematic errors. The normal place has been derived from observations of somewhat different phases, and this may greatly increase the m.e., especially where the curve has a very steep course. It is true, that just as with the Cepheids [11]) many normal places have been excluded from the discussion for this reason, but probably I did not go far enough in this procedure, so that a number of normal places were allowed to contribute to the result, whose m.e. are vitiated, i.e. increased by the systematic error indicated just now.

It may be further noted that in watching an Algol-star the observer is unfortunately often prejudiced to a certain extent; it is practically impossible to prepare for the minimum without an at least approximate knowledge of the epoch of the expected phenomenon, and it is exceedingly difficult to emancipate oneself entirely from this knowledge in making the observations.

*b*. In the second place it will be noticed that the ratio $\frac{\varepsilon_0}{\varepsilon_1}$ is 1.28 for the Algol-stars, and only 1.07 for the Cepheids. In consequence of the inevitable systematic errors $\varepsilon_0$ must be greater than $\varepsilon_1$, and I am inclined to ascribe these errors in the case of the Algol-stars chiefly to the necessity of drawing the curves smooth. Probably the m.e. $\varepsilon_0$ is not too great for the Algol-stars, but on the contrary too small for the Cepheids: and thus we arrive again at the conclusion that the curves of the Cepheids seem to follow the normal places too closely, and should have been drawn tenser.

Finally it seemed desirable to test the distribution of the errors of observation by the exponential law of GAUSS. As error of observation the deviation "observation minus normal place" was taken, increased by the deviation "normal place minus curve". Both for the Cepheids and the Algol-stars the negative and the positive errors proved to follow exactly the same law, so that the frequency curves could be drawn symmetrically. Both curves present the typical deviation from the exponential curve, consisting in an excess of the very small and of the very great errors, whereas the number of the moderately great errors is too small.

CEPHEIDS.

| Number of errors: 4288<br>m. e. ε of an observation: 0m.102 | | | | | $h = \frac{1}{\varepsilon\sqrt{2}} = 6.932$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $a$ | $n$ | $n_w$ | $n_E$ | $n_w - n_E$ | $a$ | $n$ | $n_w$ | $n_E$ | $n_w - n_E$ |
| ± 0.00 | 192 | 192 | 167 | + 25 | ± 0.22 | 39 | 31 | 33 | − 2 |
| 01 | 386 | 382 | 333 | + 49 | 23 | 22 | 25 | 26 | − 1 |
| 02 | 388 | 374 | 328 | + 46 | 24 | 19 | 22 | 22 | 0 |
| 03 | 353 | 360 | 321 | + 39 | 25 | 12 | 19 | 18 | + 1 |
| 04 | 318 | 340 | 310 | + 30 | 26 | 21 | 16 | 14 | + 2 |
| 05 | 323 | 315 | 297 | + 18 | 27 | 13 | 14 | 12 | + 2 |
| 06 | 296 | 291 | 282 | + 9 | 28 | 6 | 12 | 9 | + 3 |
| 07 | 275 | 266 | 265 | + 1 | 29 | 12 | 11 | 7 | + 4 |
| 08 | 241 | 236 | 246 | − 10 | 30 | 14 | 9 | 5 | + 4 |
| 09 | 181 | 206 | 227 | − 21 | 31 | 9 | 8 | 3 | + 5 |
| 10 | 167 | 177 | 207 | − 30 | 32 | 4 | 7 | 2 | + 5 |
| 11 | 150 | 152 | 187 | − 35 | 33 | 2 | 6 | 1 | + 5 |
| 12 | 152 | 135 | 168 | − 33 | 34 | 3 | 5 | 1 | + 4 |
| 13 | 117 | 120 | 149 | − 29 | 35 | 6 | 5 | 1 | + 4 |
| 14 | 109 | 105 | 131 | − 26 | 36 | 5 | 4 | 1 | + 3 |
| 15 | 105 | 93 | 114 | − 21 | 37 | 0 | 3 | 0 | + 3 |
| 16 | 82 | 80 | 98 | − 18 | 38 | 4 | 3 | 0 | + 3 |
| 17 | 70 | 69 | 84 | − 15 | 39 | 0 | 2 | 0 | + 2 |
| 18 | 47 | 60 | 71 | − 11 | 40 | 0 | 2 | 0 | + 2 |
| 19 | 50 | 50 | 59 | − 9 | 41 | 0 | 1 | 0 | + 1 |
| 20 | 48 | 43 | 49 | − 6 | 42 | 1 | 1 | 0 | + 1 |
| 21 | 46 | 36 | 40 | − 4 | | 4288 | 4288 | 4288 | |

$$x_1 = 0^m.070 = 0.65\,\varepsilon$$
$$x_2 = 0\ .240 = 2.36\,\varepsilon$$

## ALGOL-STARS.

Number of errors: 9955
m. e. $\varepsilon$ of an observation: $0^m.132$

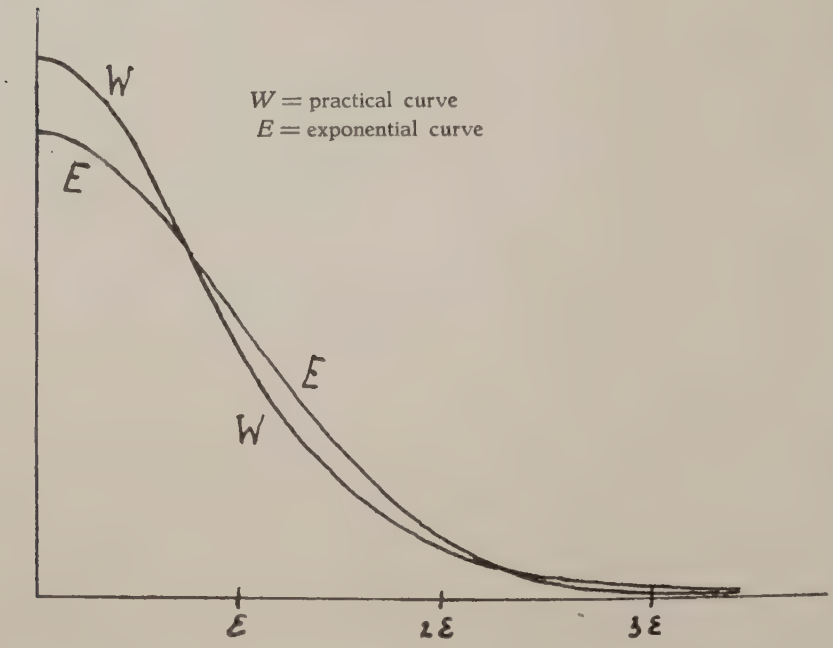
$h = \frac{1}{\varepsilon\sqrt{2}} = 5.348$

| $a$ | $n$ | $n_w$ | $n_E$ | $n_w - n_E$ | $a$ | $n$ | $n_w$ | $n_E$ | $n_w - n_E$ |
|---|---|---|---|---|---|---|---|---|---|
| ± 0.00 | 335 | 340 | 300 | + 40 | ± 0.34 | 29 | 32 | 22 | + 10 |
| 01 | 712 | 676 | 600 | + 76 | 35 | 26 | 28 | 18 | + 10 |
| 02 | 632 | 670 | 593 | + 77 | 36 | 26 | 24 | 15 | + 9 |
| 03 | 588 | 650 | 585 | + 65 | 37 | 28 | 21 | 12 | + 9 |
| 04 | 589 | 622 | 574 | + 48 | 38 | 16 | 18 | 9 | + 9 |
| 05 | 601 | 595 | 559 | + 36 | 39 | 11 | 16 | 8 | + 8 |
| 06 | 543 | 566 | 542 | + 24 | 40 | 12 | 14 | 6 | + 8 |
| 07 | 597 | 530 | 523 | + 7 | 41 | 6 | 12 | 5 | + 7 |
| 08 | 517 | 492 | 499 | − 7 | 42 | 14 | 11 | 4 | + 7 |
| 09 | 458 | 457 | 477 | − 20 | 43 | 6 | 9 | 3 | + 6 |
| 10 | 426 | 421 | 451 | − 30 | 44 | 15 | 8 | 2 | + 6 |
| 11 | 400 | 385 | 425 | − 40 | 45 | 6 | 6 | 2 | + 4 |
| 12 | 335 | 349 | 397 | − 48 | 46 | 3 | 4 | 2 | + 2 |
| 13 | 336 | 315 | 371 | − 56 | 47 | 6 | 4 | 1 | + 3 |
| 14 | 263 | 287 | 344 | − 57 | 48 | 7 | 4 | 1 | + 3 |
| 15 | 292 | 263 | 314 | − 51 | 49 | 2 | 3 | 1 | + 2 |
| 16 | 252 | 239 | 289 | − 50 | 50 | 8 | 3 | 1 | + 2 |
| 17 | 228 | 219 | 265 | − 46 | 51 | 2 | 3 | 0 | + 3 |
| 18 | 175 | 201 | 237 | − 36 | 52 | 1 | 3 | 0 | + 3 |
| 19 | 179 | 183 | 214 | − 31 | 53 | 2 | 2 | 0 | + 2 |
| 20 | 179 | 165 | 191 | − 26 | 54 | 4 | 2 | 0 | + 2 |
| 21 | 150 | 150 | 171 | − 21 | 55 | 1 | 2 | 0 | + 2 |
| 22 | 147 | 136 | 150 | − 14 | 56 | 2 | 2 | 0 | + 2 |
| 23 | 116 | 123 | 132 | − 9 | 57 | 1 | 2 | 0 | + 2 |
| 24 | 113 | 110 | 116 | − 6 | 58 | 0 | 1 | 0 | + 1 |
| 25 | 84 | 98 | 101 | − 3 | 59 | 1 | 1 | 0 | + 1 |
| 26 | 89 | 87 | 87 | 0 | 60 | 0 | 1 | 0 | + 1 |
| 27 | 80 | 78 | 74 | + 4 | 61 | 4 | 1 | 0 | + 1 |
| 28 | 57 | 69 | 64 | + 5 | 62 | 1 | 1 | 0 | + 1 |
| 29 | 73 | 61 | 54 | + 7 | 63 | 0 | 1 | 0 | + 1 |
| 30 | 49 | 53 | 46 | + 7 | 64 | 0 | 0 | 0 | 0 |
| 31 | 36 | 47 | 39 | + 8 | 65 | 1 | 0 | 0 | 0 |
| 32 | 39 | 41 | 32 | + 9 |  | 9955 | 9955 | 9955 |  |
| 33 | 44 | 36 | 27 | + 9 |  |  |  |  |  |

$x_1 = 0^m.076 = 0.58\,\varepsilon$

$x_2 - 0\ .260 = 1.97\,\varepsilon$

In the tables (see p. 146 and p. 147) the actually observed numbers $n$ are given, graphically smoothed down to $n_w$; they have been compared with the values $n_\varepsilon$ following from the exponential law. The errors 0.00, 0.01, 1.02 etc. are supposed to lie between the limits 0.00 and $0.00^5$, $0.00^5$ and $0.01^5$, $0.01^5$ and $0.02^5$ etc.



The tables show first that, in accordance with the greater m.e., the greater extreme cases occur with the Algol-stars. It may seem strange that it is possible to make errors of $0^m.5$ and $0^m.6$, but according to the law of the great numbers such extreme cases, more than four times the m.e., must now and then occur in a series of almost 10.000 observations. In the second place we may remark, that for the Cepheid series the abscissae*) of the points of intersection of the exponential with the actually observed curve almost entirely satisfy the remarkable equation 12):

$$\left(\frac{x}{\varepsilon}\right)^2 - 6\left(\frac{x}{\varepsilon}\right) + 3 = 0.$$

From this it follows:

$$\left.\begin{array}{l} x_1 = 0.74\,\varepsilon = 0^m.076 \\ x_2 = 2.33\,\varepsilon = 0^m.238 \end{array}\right\} \text{for } \varepsilon = 0^m.102,$$

the observed points of intersection lying at $0^m.070$ and $0^m.240$. For the Algol-stars $\varepsilon = 0^m.132$, hence the points of intersection would be expected at

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*) Here the positive values are only considered.

$0^m.098$ and $0^m.308$, whereas they are really found at $0^m.076$ and $0^m.260$. That both points lie so much nearer the *Y*-axis than follows from the above equation may be ascribed — as is evident from the figure — to a too small number of small errors (smaller than that actually observed, though still much greater than the theoretical number) and a too great number of great errors. This may readily be ascribed to the influence of the systematic errors "normal place minus curve", which give rise to considerable corrections in the Algol-curves, since they must necessarily be drawn smooth.

## CONCLUSION.

Apart from two exceptional cases there is no urgent reason, why the curves of the examined Cepheids should not be drawn perfectly smooth and tense. The remaining errors appear to behave — in a still greater degree than those of the Algol-curves — entirely as accidental errors. If, as many observers assert, there is hardly question of a mean curve at all for the Cepheids on account of the numerous irregularities of all kinds, these irregularities are entirely hidden in the errors of observation; they do not spoil their accidental character, nor do they appreciably increase their amount.

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8. Astr. Nachr. **184,** 248 (1910).
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12. Compare the paper by BESSEL, Astr. Nachr. **15,** 397 (1838) and that of SCHOLS, Verslag der vergadering van 28 April 1893, Kon. Akademie v. Wet., p. 195.

**Physics.** — *"The Evershed effect in the spectrum of sun-spots"*. By Prof. W. H. JULIUS[1]).

(Communicated at the meeting of January 31, 1925).

A well-defined general property of Fraunhofer lines is their systematic deformation in the spot-spectrum, known as the „Evershed effect".

About 1909 EVERSHED observed[2]) that, if the slit of the spectrograph bisects a sun-spot in a direction passing through the centre of the solar disc, the lines of the spot-spectrum are systematically displaced, towards the red at the peripheral edge, towards the violet at the central edge of the spot. These displacements are small if the spot is located not far from the centre of the disc and increase as the limb is approached; their magnitude depends in a special manner upon the intensity of the lines and increases in general with the wave-length, but not proportionally. If the slit cuts the spot in other directions, similar displacements are observed, though smaller and less systematic; least when the slit is perpendicular to the radius of the disc. The hydrogen line $H\beta$ did not show the displacement, and a few other strong chromospheric lines seemed to be displaced in a direction opposite to the regular shift[3]).

It is known that EVERSHED has interpreted these phenomena as indicating motion of the absorbing gases from the umbra radially outwards, tangential to the solar surface, with velocities that increase until the outer limit of the penumbra is reached, where the motion is rather abruptly stopped.

This interpretation seemed to account fairly well for the principal characteristics of the phenemenon. It is accepted and elaborated in detail by ST. JOHN[4]) using a rich observational material collected on Mount Wilson in addition to the original Kodaikanal data. If one holds the view — taken by both observers — that the solar spectrum is a pure absorption phenomenon, it seems in fact impossible to explain the Evershed effect without having recourse to the Doppler principle; other causes of line displacement, like pressure, electric or magnetic fields, cannot in any satisfactory way be made responsible for the peculiarities of the phenomenon.

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[1]) Soon after deliverance of the proof of this paper to Prof. JULIUS for correction for press, the Academy, to its great sorrow, received the announcement of his death on April 15, 1925.

[2]) EVERSHED, Kodaikanal Bulletin XV, 1909.

[3]) In still another respect the lines $H_\alpha$ of hydrogen and $H$ and $K$ of calcium behave differently from the rest: their displacement begins over the photosphere, outside the penumbral region, and is not always very clearly defined, owing to the width and irregularities at the edges of the line (Transactions of the International Union for co-operation in solar Research, Vol. IV, p. 129—130). Circumstances regarding those lines evidently require separate consideration.

[4]) ST. JOHN, Contrib. Mt. Wilson Obs. N⁰. 69 and 74; Astroph. Journ. **37**, 322, **38**, 341, 1913.

But now it had to be ascertained how far the necessary consequences of that Doppler explanation would prove compatible with the results of further observations, for instance with the fact that over spot umbrae the displacements are very small and uncertain in direction, nay indicating descent in the majority of cases. That serious difficulties are here encountered, I believe to have sufficiently shown on a former occasion [1]), to justify the attempt to give due attention to an entirely different interpretation of the phenomenon.

It is indeed not necessary to suppose that the darkness of Fraunhofer lines is caused by absorption alone. We may keep in view the possibility that in the solar spectrum we are dealing with *dispersion lines* [2]), in which the distribution of the light is governed by the sinuosity of rays in a medium, the optical density of which varies very irregularly in general — but rather systematically in the regions of sun-spots.

On the basis of this hypothesis too an interpretation of the Evershed effect, accounting for its most characteristic features, could be given. As a substitute for the dynamical conception of the spot, with its permanent hurricanes of many kilometers per second wind velocity — required by the absorption theory — the dispersion hypothesis introduces a rather statical conception, in which differences of density and composition determine the optical phenomena, and motion may be much slower [3]).

After the ample observations communicated by ST. JOHN in the years 1913—1915 not many new data on the Evershed effect have appeared; only one important article, published by EVERSHED himself in *Kodaikanal*

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[1]) JULIUS, Astroph. Journ. **40**, 1, 1914; **43**, 43, 1916.

[2]) In support of this theory of the solar spectrum we call to mind the following results of recent inquiry: 1. The new ideas on atomic structure are also leading to the view that the spectral regions where true absorption can take place are much narrower than was formerly believed (BOHR, Zeitschr. f. Phys. **13**, 162, 1923). 2. At all levels in the sun where Fraunhofer lines are supposed to originate, the pressure must be very low, much less than 1 atm. (ST. JOHN and BABCOCK, Astroph. Journ. **60**, 32, 1924). 3. For the limb-centre displacements no other explanation besides the one following from the dispersion theory seems to hold (JULIUS, Zeitschr. f. Phys. **27**, 23, 1924). 4. In an article on "Ionisation in stellar atmospheres" A. PANNEKOEK also concludes that in addition to selective absorption and molecular scattering there must be active in the sun another cause of extinction, at least ten times as effective as molecular scattering (B. A. N. **19**, 1922, p. 113). 5. From the defect of perspective foreshortening in spectro-heliograms (These Proceedings **27**, 451, 1924), and from stereoscopic observation of such documents we may infer that the photosphere must be transparent down to considerable depth.

[3]) From this point of view the Evershed effect has for the first time been dealt with in these Proceedings **12**, p. 278—279, 1910; more amply in Astroph. Journ. **40**, 1—32, 1914, and **43**, 43—66, 1916. The idea was then opposed by ST. JOHN, in Contrib. Mt. Wilson Nos 93 and 123 or Astroph. Journ. **41**, 28, 1915 and **44**, 1916, and again defended by the author in several articles on the dispersion theory of Fraunhofer lines (Verslag Akad. v. Wet. Amsterdam, **25**, 1245, 1917; These Proceedings **23**, p. 1113, 1921; **26**, p. 329, 1923; Astroph. Journ. **54**, 92, 1921).

*Bull.* **51**, 1916, has yet revealed certain peculiarities of the phenomenon which one has to keep in mind in any attempt to explanation. EVERSHED, in fact, adheres to the interpretation of the displacements as Doppler effects, but not without calling attention to some difficulties to which this leads.

The new data we have to consider bear upon a large spot which crossed the disc in 21° northern latitude between March 29th and April 12th 1915. The seeing was excellent. EVERSHED emphasizes that the displacements are larger with good definition of the penumbral image than would have been the case with an image more or less diffused along the slit by poor definition or long exposure time. So the characteristics of the phenomenon could be more sharply noticed than on former occasions. The computed horizontal radial velocities were found about 2.7 times larger than those observed by ST. JOHN for the corresponding line intensities — a discrepancy which is probably mainly accounted for by difference in magnitude of the observed spots or by unequal diffusion of the spot image on the slit-plate.

It was an important feature of these observations that the displacements have been measured *separately* at the opposite outer limits of the penumbra, each with respect to the average position of the line outside the spot (whereas ST. JOHN only gave the sums of the opposite displacements). Selected for measurement were a great many *Fe*-lines of intensities ranging from 0 to 6 of ROWLAND's scale, and besides a few lines of *Ni*, *Cr*, and *Ti*. The spot passed the meridian on April 4—5; several spectra were obtained before and after that passage and measurements made on 11 plates in total.

The known relation between the magnitude of the displacements and the line intensity showed quite clearly again; the shifts were greatest for intensities 0 and 1; they decreased as the intensities rose to 5 and 6. Moreover, a remarkable fact presented itself, which had not been noticed before: viz. that *the displacements were systematically greater in the penumbra directed towards the limb.* As on that side the shift is always towards the red, we may also state: *the displacements towards the red were systematically greater than those towards the violet.*

EVERSHED gives no explanation of this remarkable fact; he suggests that it may be an accidental circumstance, although the same phenomenon appears on some of his previous measures. The following table shows clearly, though, that the inequality is considerable and holds for all line intensities. Mean results are here given of a great number of observations relating to different positions of the spot on the disc and to various spectral regions. The figures represent kilometers per second, reduced to horizontal movement at the outer edges of the penumbra; the positive sign corresponds to receding motion.

On the basis of the Doppler interpretation we are thus led to the enigmatic conclusion that in the spot there would always be an excess of motion directed towards the limb of the solar disc. It appears impossible to conceive a circulatory process answering that peculiar condition, whatever vertical velocity components one might imagine for complementing the radial motion. This impossibility condemns the radial motion hypothesis.

| | April 3, Spot East | | April 6 and 7, Spot West. | |
|---|---|---|---|---|
| Line intensity | East penumbra | West penumbra | East penumbra | West penumbra |
| 0 en 1 | + 2,73 | — 2,02 | — 1,41 | + 3,23 |
| 2 | + 2,19 | — 2,04 | — 1,21 | + 2,84 |
| 3 | + 2,14 | — 1,59 | — 1,08 | + 2,49 |
| 4 | + 2,02 | — 1,66 | — 1,06 | + 2,39 |
| 5 en 6 | + 1,09 | — 1,41 | — 0,90 | + 1,98 |

We are going to show that the dispersion theory of Fraunhofer lines suggests an adequate explanation of the observed peculiarity.

First, however, we should mention a few remarks made by Evershed with regard to line displacements observed when the slit was perpendicular to the radius of the solar disc.

On April 1 (spot near east limb) a shift was observed towards the red in the southern penumbra only; interpreted as a horizontal movement it would indicate a velocity of 0.64 km/sec. Two hours later: nearly equal displacements in north and south penumbrae, both about 0.46 km/sec.

On April 2 the same spot showed displacement towards the red at its northern edge only, corresponding to 0.9 km/sec. horizontal velocity; in the southern penumbra there was a slight shift towards the violet, 0.1 km/sec.

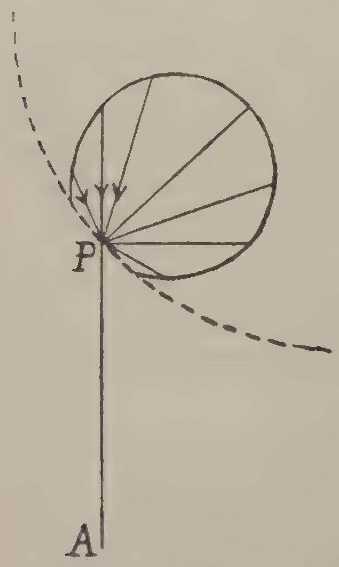
These displacements cannot represent a rotational movement of the spot, as the northern and southern shifts are not opposite. After the spot had passed the meridian, on April 9, a similar exposure with tangential slit gave, however, fairly opposite displacements north and south; reduced to horizontal movement:

northern penumbra: 0.65 km/sec.,
southern penumbra: — 0.88 km/sec.

Let us now suppose that this does represent a rotation, with a mean velocity of 0.77 km/sec. at the outer edge of the penumbra. The diameter of the spot was 41000 km.; a complete rotation would have taken 46 hours; so one might have expected a visible rotation of the (irregular) spot in a reasonable time. There was, however, no evidence of such change, when comparing the shape of the spot on successive days. Moreover, the direction of the rotation would not correspond to that found by Hale from the magnetic polarity of the spot. Evershed, therefore, considers it to be doubtful whether these line displacements really indicate rotation of the gases over the spot; he can only ascribe them to fortuitous, irregular movements.

It deserves notice that neither about the origin, nor about the consequences of violent solar storms (rotational or radial) any other evidence besides line displacement has ever been given by the observations. The circulatory system imagined by Evershed and St. John cannot, therefore, be said to constitute a necessary link in some series of conceptions; it depends entirely on the arbitrary hypothesis that the shifts are a Doppler effect. So we may safely abolish that supposition if we can dispense with it, as no connexion with other phenomena is thus broken.

Let us now consider the matter from the point of view of the dispersion theory. We start from the conception that in a sun-spot the optical density varies altogether irregularly, but increases on the average from the umbra outwards. Such a distribution of matter, existing in front of a luminous sphere, must show a peculiar distribution of light much like the known aspect of the umbra and penumbra of a sunspot. This could easily be explained geometrically using simple diagrams, and demonstrated by means of experiments with liquid drops of different refractive power[1]) and with whirling masses of gas[2]). From this conception of the nature of a sun-spot follows immediately, without any additional hypothesis, an explanation of the shifts of the Fraunhofer lines in the spot spectrum; we only have to take into account the unequal refractivity of the *R*-light and the *V*-light in the surroundings of each absorption line, and the characteristics of the Evershed effect will at once become manifest [3]).



The following representation of the rather intricate refracting process appeals perhaps somewhat more to the mind than the one given on former occasions, though it essentially rests on exactly the same principle.

Let *P* be a point somewhere in the solar atmosphere. It receives light from the various directions in quantities proportional to the radii vectores of the „surface of irradiation" [4]) (the mean shape of which is known from direct measurement of the distribution of brightness over the solar disc). We have to consider the properties of the light which, after having suffered irregular refraction in the region about *P*, emerges in the direction *PA* towards the earth. As regards the position of *P* in the spot region we distinguish the following two cases:

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[1]) These Proceedings **12**, 206, 1909.

[2]) Physik. Zeitschr. **15**, 48, 1914.

[3]) Astroph. Journ. **40**, (especially p. 19—25) 1914, and **43**, 43—66, 1916.

[4]) Handwörterbuch d. Naturwissenschaften VII. 830, 1912.

*a*. *P* is situated in the penumbra nearest to the sun's limb. According to our supposition the density is everywhere irregular, so that there are gradients in all directions. A gradient will be designated + or — if the density is either increasing or diminishing towards the edge of the disc.

Consider the action of an arbitrary + gradient on a certain *R*-light and a certain *V*-light, selected so as to have equal values of $n-1$. Then the *R*-light must have come from the left, the *V*-light from the right side; and, owing to the peculiar shape of the surface of irradiation, we immediately see that the weakening suffered by the *R*-light must be somewhat greater than the strengthening of the *V*-light.

Next consider the action of an arbitrary — gradient on the same selected kinds of light. Now, with equal angular deviations, the weakening of the *V*-light will be more considerable than the strengthening of the *R*-light.

In both cases, therefore, if *R*-light and *V*-light are taken together, the joint result is a weakening. But because *P* is in the peripheral half of the penumbra, where the + gradients are on the average higher than the — gradients, the weakening of the *R*-light will be greater than the weakening of the *V*-light. This manifests itself as a displacement of the line towards the red.

*b*. *P* be situated in the penumbra farthest from the sun's edge. We again distinguish the case of a + gradient and a — gradient, and find once more that the weakening always predominates. At present, however, we are dealing with a region where the — gradients have the advantage over the + gradients, and where, therefore, the *V*-light will be more weakened than the *R*-light; the line appears to be shifted towards the violet.

The principal feature of the Evershed effect is thus accounted for. But what about the peculiarity afterwards stated, that on the peripheral edge of the spot the displacements are always greater than on the central edge?

This result too is easily understood on the basis of the dispersion theory. We are concerned with a consequence of the same circumstance upon which also depend the general displacement of Fraunhofer lines towards the red, and the limb—centre displacements in particular.

Indeed, the intensity of refraction effects is determined, for each wavelength, by the corresponding value of $n-1$. This quantity varies strongly in passing every absorption line; but as on an average the refractive index of the solar gases is greater than 1, the absolute value of $n-1$ will, as a rule, be greater on the red than on the violet sides of the absorption lines. And stronger irregular refraction generally involves increased weakening; so the average value of the shifts towards the red must exceed that of the shifts towards the violet.

It is interesting to notice that this single principle — which causes Fraunhofer lines to be asymmetrical to a degree fluctuating through the spectrum — correlates several classes of systematic line displacements, namely the general sun-arc displacements, the limb-centre shifts, and the preponderance of displacements towards the red in the Evershed effect. A very marked excess of displacements towards the red has also been found in prominences both at the limb and in disturbed regions on the disc [1]; it is not improbable that this is due to the same cause.

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[1] Transactions of the International Union for co-operation in Solar Research, Vol. IV, p. 128, 1914.

## **Chemistry.** — "*Equilibria in systems, in which phases, separated by a semi-permeable membrane.*" IV. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of December 27, 1924.)

### *Ternary equilibria with solid phases.*

In the previous communication we have discussed the *O.W.A.* (osmotic water-attraction) etc. of liquids in ternary systems, when one of the components occurs as solid phase. Now we shall assume that a binary compound viz. a hydrate component $Y$ occurs.

The saturation-curve of this hydrate is represented for a definite $T$ and $P$ by curve $w\,d\,v$; point $H$ represents the hydrate; every straight line starting from point $H$ is allowed to intersect this curve in one point only. We shall call $w$ the terminating-point of the curve rich in water and $v$ the terminating-point poor in water. Just as in the previous communication we shall say also here that point $a$ is situated closer to $w$ than $b$, etc. It is not allowed, however, to prove from this (compare the previous communication) that a liquid of this curve contains the more (less) water, the closer (further) it is situated to (from) the point $w$. The dotted curves $w\,m$, etc. are the isotonic $W$-curves.

In a similar way as in the previous communication we may deduce:

$1^0$. An isotonic curve and the saturation-curve of the hydrate can intersect one another in one point only, they never can touch one another.

$2^0$. The *O.W.A.* of a liquid of a saturation-curve of a hydrate is greater (smaller) the more this liquid is situated further from (closer to) the terminating-point rich in water of this curve.

The *O.W.A.* increases, therefore, along curve $w\,v$ in the direction of the arrows.

$3^0$. An isotonic curve and the saturation-curve of a hydrate are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle. When the one curve touches one side of that angle, than the other curve touches the other side.

In point $c$ (fig. 1) the conjugation-angle is $WcH$; as the saturation-curve touches $WC$ in $c$, the isotonic curve $n\,n'$ must touch $cH$ in $c$.

We are able to deduce the property mentioned sub. $2^0$ a.o. also in the following way. When we represent the composition of $H$ by: $\beta\, Mol\, Y + (1-\beta)\, Mol\, W$, then the saturation-curve $w\,v$ is defined by:

$$\zeta - x\frac{\delta\zeta}{\delta x} + (\beta - y)\frac{\delta\zeta}{\delta y} = \zeta_H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $\zeta_H$ is the $\zeta$ of the substance $H$. The *O.W.A.* of a liquid is defined by:

$$\varphi = \zeta - x\frac{\delta\zeta}{\delta x} - y\frac{\delta\zeta}{\delta y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) follows:

$$[-xr + (\beta - y)s]\,dx + [-xs + (\beta - y)t]\,dy = 0 \quad . \quad . \quad . \quad (3)$$

From (2) follows in connection with (3)

$$\frac{1}{\beta}\,d\varphi = -s\,dx - t\,dy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We now take a system of coordinates with the point $H$ as pole and the line $HW$ as axis; we represent the radius vector by $\varrho$ and the angle by $\mu$; consequently in $w$ is $\mu = 0$, in $v$ is $\mu = 180°$. In order to simplify the calculation we imagine angle $WXY = 90°$, which has not any influence on the result. We now have:

$$\varrho \sin\mu = x \qquad \varrho\cos\mu\,.\,d\mu + \sin\mu\,.\,\delta\varrho = dx$$

$$\varrho\cos\mu = \beta - y \qquad -\varrho\sin\mu\,.\,d\mu + \cos\mu\,.\,\delta\varrho = -\delta y.$$

When we substitute those values in (3) and (4) then follows:

$$\left.\begin{aligned} \varrho\,[(t - r)\sin\mu\,.\,\cos\mu\,. + s(\cos^2\mu - \sin^2\mu)]\,d\mu = \\ = [r\sin^2\mu - 2s\sin\mu\cos\mu + t\cos^2\mu]\,d\varrho \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{1}{\beta}\,.\,\delta\varphi = -\varrho\,(s\cos\mu + t\sin\mu)\,d\mu - (s\sin\mu - t\cos\mu)\,\delta\varrho \,. \quad . \quad (6)$$

Outside a region of dimixtion $rt - s^2$ and consequently also the coefficient of $\delta\varrho$ in (5) is always positive and never zero; therefore $\delta\mu$ can not become zero. A radius vector going through point $H$, therefore never can touch the saturation-curve $wv$, only in one point it may intersect this curve.

By elimination of $\delta\varrho$ it follows from (5) and (6):

$$\frac{d\varphi}{d\mu} = -\frac{\beta\varrho\,(rt - s^2)\sin\mu}{r\sin^2\mu - 2s\sin\mu\cos\mu + \cos^2\mu} \quad . \quad . \quad . \quad . \quad (7)$$

so that the second part of (7) is negative. Consequently $\varphi$ decreases along curve $wv$ starting from $w$ towards $v$, so that *O.W.A.* increases starting from $w$ towards $v$.

Point $c$, viz. the point of contact of the tangent to curve $wv$ drawn from point $W$, divides $wv$ into two parts. We now bring into osmotic contact two liquids $L_a$ and $L_b$ of part $wc$; as $L_b$ has a greater *O.W.A.* than $L^a$, water is diffussing from $L_a$ towards $L_b$. Consequently the inversion is:

$$\left(L_a \overset{|}{\underset{|}{\rightarrow}} L_b\right) \rightarrow \left(\text{solid } H + L_q \overset{|}{\underset{|}{\longleftrightarrow}} L_r\right) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In this $L_q$ represents a saturated solution between $a$ and $b$ and $L_r$ an unsaturated solution; of course $L_q$ and $L_r$ are situated on the same osmotic curve.

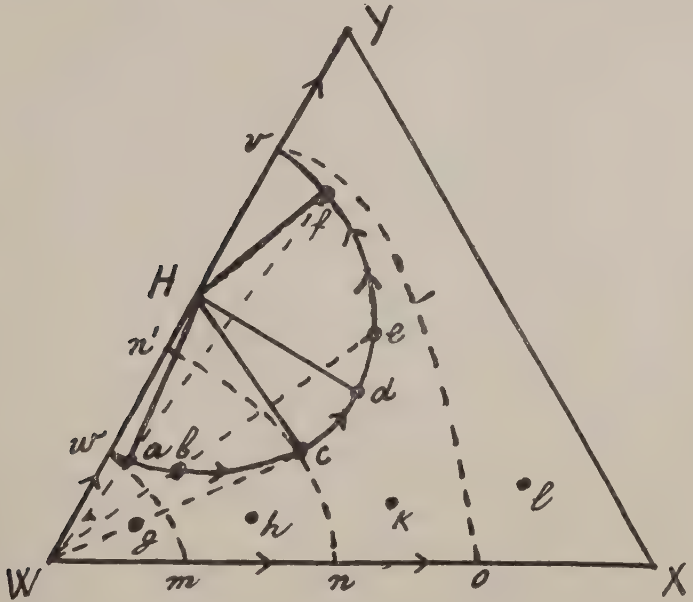

Fig. 1.

When we bring into osmotic contact $L_e$ and $L_f$ of part $cv$, then the inversion is:

$$\left(L_e \overset{|}{\underset{|}{\rightarrow}} L_f\right) \rightarrow \left(L_s \overset{|}{\underset{|}{\longleftrightarrow}} L_t + solid\ H\right) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which $L_t$ represents a liquid between $e$ and $f$ and $L_s$ an unsaturated liquid.

When we take two liquids, the one of which is situated on part $wc$ and the other on part $cv$, f.i. $L_b$ and $L_f$, then the inversion is:

$$\left(L_b \overset{|}{\underset{|}{\rightarrow}} L_f\right) \rightarrow \left(solid\ H + L_u \overset{|}{\underset{|}{\longleftrightarrow}} L_u + solid\ H\right) \quad . \quad . \quad . \quad (10)$$

The position of $L_u$ depends on the situation of the complex of $L_b$ and $L_f$; when f.i. this complex is situated on the line $Hd$, then is $L_u = L_d$.

With inversion (8) the solid substance arises on that side of the membrane on which water is removed from; in (9) on that side to which water is diffusing; in (10) the solid substance arises on both sides of the membrane.

We bring the two binary liquids $L_w$ and $L_v$ into osmotic contact. As $L_v$ has a greater $O.W.A.$ than $L_w$ the inversion is:

$$\left(L_w \overset{|}{\underset{|}{\rightarrow}} L_v\right) \rightarrow \left(\text{solid } H + L_w \;\Big|\; \text{solid } H\right) \quad . \;\; . \;\; . \;\; . \quad (11)$$

or:

$$\left(L_w \overset{|}{\underset{|}{\rightarrow}} L_v\right) \rightarrow \left(\text{solid } H \;\Big|\; L_v + \text{solid } H\right) \quad . \;\; . \;\; . \;\; . \quad (12)$$

In both cases viz. water is diffusing from $L_w$ towards $L_v$ and $L_w$ passes with loss of water, $L_v$ with increase of water into solid $H$. This diffusion continues till all the liquid either on the one or on the other side of the membrane, has disappeared. When we bring $L_w$ and $L_v$ in definite ratio into osmotic contact, then the inversion may become also:

$$\left(L_w \overset{|}{\underset{|}{\rightarrow}} L_v\right) \rightarrow \left(\text{solid } H \;\Big|\; \text{solid } H\right) \quad . \;\; . \;\; . \;\; . \;\; . \quad (13)$$

The liquids then disappear on both sides of the membrane with separation of solid $H$.

We now bring into osmotic contact $L_w$ with a liquid $L_q$; consequently we have a system $\left(L_w \;\Big|\; L_q\right)$. In the same way as in the previous communication it now appears:

1⁰. when $L_q$ is situated within the region $Wwm$, then water is diffusing from $L_q$ to $L_w$; then $L_w$ passes into an unsaturated liquid between $w$ and $W$.

2⁰. when $L_q$ is situated on the isotonic curve $wm$, then $L_q$ and $L_w$ are in osmotic equilibrium and nothing happens.

3⁰. when $L_q$ is situated within the region $w\,m\,X\,Y\,v\,d\,w$, then water is diffusing from $L_w$ to $L_q$; then $L_w$ shall separate the substance $H$ and shall dry up totally or partially.

When we bring $L_v$ into osmotic contact with a liquid $L_q$, then we have to bear in mind that, as appears also from fig. 1, $L_v$ separates the solid hydrate $H$ with increase of water, and that $L_v$ passes into an unsaturated solution losing water.

We now find:

1⁰. when $L_q$ is situated within the region $W\,o\,v\,d\,w\,W$, then water is diffusing from $L_q$ to $L_v$; then $L_v$ separates solid $H$ and dries up totally or partially.

2⁰. when $L_q$ is situated on the isotonic curve $v\,o$ then nothing happens.

3⁰. when $L_q$ is situated within the region $v\,o\,X\,Y$ then water is diffusing from $L_v$ to $L_q$; then $L_v$ becomes an unsaturated solution between $v$ and $Y$.

Different results may be deduced from those considerations. A.o. this: all liquids within the region $w\,m\,o\,v\,d\,w$ make as well $L_w$ as $L_v$ to dry up totally or partially into the solid substance $H$.

In accordance with our definition of the osmotic water-attraction of solid substances (see the previous communication) we have to mean by the *O.W.A.* of the hydrate *H* the *O.W.A.* of the liquid which arises when a very small quantity of water is added to the substance *H*; consequently here this is the liquid $L_w$. Therefore curve *w m* is the curve $(O.W.A. = H)$.

Just as in the previous communication we now find:

1⁰. the hydrate *H*, in osmotic contact with a liquid within the region *W w m*, shall remove water from this liquid.

2⁰. the hydrate *H*, in osmotic contact with a liquid outside the region *W w m*, can not remove water from this liquid.

Consequently when we bring solid *H* in osmotic contact with liquid $L_g$ (fig. 1) then water diffuses to the solid substance and is formed either: solid $H + L_w$ or an unsaturated liquid between *w* and *W*.

When we bring solid *H* in osmotic contact with one of the liquids *h, k, l, n* or *o* (fig. 1) then nothing happens. When, however, we bring in osmotic contact one of those liquids with $L_w$, then $L_w$ is drying up totally or partially with separation of solid *H*.

In fig. 2 point *D* represents a ternary compound, f.i. a hydrous double-salt. The saturation-curve of *D* is represented by the closed curve *w b v f w*. In accordance with a well-known property all lines starting from point *D* intersect this curve in one point only. As *w* and *v* represent the solutions of *D* in pure water, we may call *w* the point of solubility of substance *D* rich in water and *v* the point poor in water

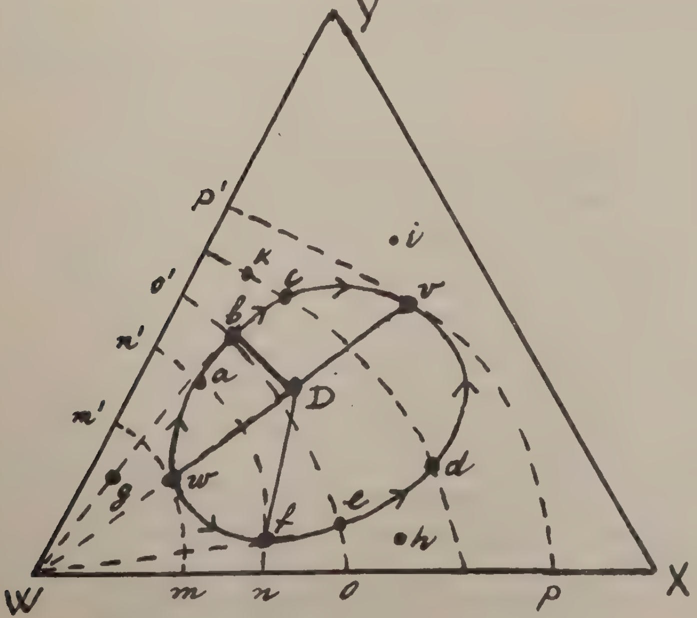

Fig. 2.

Further we shall call $w\,b\,v$ the branch of the saturation-curve rich in $Y$ and $w\,f\,v$ the branch rich in $X$. The dotted curves $mm'$, $nn'$, etc. are isotonic curves.

We now easily may deduce:

1⁰. An isotonic curve intersects the saturation-curve of a ternary compound in two points; the one point of intersection is situated on the branch rich in $X$, the other on the branch rich in $Y$. The isotonic curves going through $w$ and $v$ touch the saturation-curve in $w$ and $v$.

Consequently with each solution of the branch rich in $X$, a definite solution of the branch rich in $Y$ may be in osmotic equilibrium; f. i. $L_a$ with $L_f$, $L_b$ with $L_e$, $L_c$ with $L_d$ etc.

2⁰. The $O.W.A.$ of a liquid of the saturation-curve is greater (smaller) the more it is situated further from (closer to) the point $w$.

Consequently the $O.W.A$ increases on both branches of the curve in the direction of the arrows.

3⁰. For an isotonic curve and the saturation-curve of a ternary substance in the vicinity of their point of intersection the same is true as for an isotonic curve and the saturation-curve of a component or of a hydrate.

Consequently the curves $nn'$ and $oo'$ must touch the lines $fD$ and $bD$ in $f$ and $b$.

We also may deduce the property, mentioned sub 2⁰, a. o. in the following way. We represent the composition of $D$ by: $\alpha$ $Mol\ X + \beta$ $Mol\ Y + (1-\alpha-\beta)$ $Mol\ W$. Then the saturation-curve $wv$ is defined by:

$$\zeta + (\alpha - x)\frac{\delta\zeta}{\delta x} + (\beta - y)\frac{\delta\zeta}{\delta y} = \zeta_D \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which $\zeta_D$ is the $\zeta$ of the solid substance $D$. The $O.W.A.$ of a liquid is defined by:

$$\varphi = \zeta - x\frac{\delta\zeta}{\delta x} - y\frac{\delta\zeta}{\delta y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

It follows from (14):

$$[(\alpha - x)\,r + (\beta - y)\,s]\,dx + [(\alpha - x)\,s + (\beta - y)\,t]\,dy = 0. \quad . \quad (16)$$

From (15) follows, in connection with (16):

$$d\varphi = -(\alpha r + \beta s)\,dx - (\alpha s + \beta t)\,dy \quad . \quad . \quad . \quad . \quad . \quad (17)$$

We now take a system of coordinates, the pole of which is represented by point $D$, the axis by the line $DW$. We let the radius vector to turn at increasing value of $\mu$ in the direction of the hands of a clock, consequently starting from $w$, along $a$, $b$, $c$ towards $v$ and backwards along $d$ towards $w$. When we put angle $DWX = \vartheta$ and when we take for the sake of simplicity angle $XWY = 90°$, then we have:

$$\alpha - x = \varrho\cos(\mu - \vartheta) \qquad \beta - y = -\varrho\sin(\mu - \vartheta)$$

$$dx = \varrho\sin(\mu - \vartheta)\,.\,d\mu - \cos(\mu - \vartheta)\,\delta\varrho$$

$$dy = \varrho\cos(\mu - \vartheta)\ \ d\mu + \sin(\mu - \vartheta)\,.\,\delta\varrho$$

Substituting those values in (16) and (17) and putting $\mu - \vartheta = \mu'$, then we find;

$$\left.\begin{aligned} \varrho\,[(r-t)\sin\mu'\cos\mu' + s\,(\cos^2\mu' - \sin^2\mu')]\,d\mu = \\ = [r\cos^2\mu' - 2\,s\sin\mu'\cos\mu' + t\sin^2\mu']\,\delta\varrho \end{aligned}\right\} \quad . \quad . \quad (18)$$

$$d\varphi = -\varrho[R\sin\mu' + S\cos\mu']\,d\mu + [R\cos\mu' - S\sin\mu']\,d\varrho \quad . \quad (19)$$

in which:

$$R = ar + \beta s \qquad \text{and} \qquad S = as + \beta t$$

From (18) again follows the same as is deduced from (5). When we eliminate $d\varrho$ from (18) and (19) and when we substitute again $\mu'$ by $\mu - \vartheta$, then follows:

$$\frac{d\varphi}{d\mu} = -\frac{\varrho\,(rt - s^2)\,[a\sin(\mu - \vartheta) + \beta\cos(\mu - \vartheta)]}{A} \quad . \quad . \quad . \quad (20)$$

in which $A$ represents the coefficient of $d\varrho$ from (18). As further:

$$\frac{\beta}{a} = tg\,\vartheta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

(20) passes into:

$$\frac{d\varphi}{d\mu} = \frac{-\varrho\,(rt - s^2)\,a\sin\mu}{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Consequently $\varphi$ is maximum or minimum for $\sin\mu = 0$, therefore when $\mu = 0°$ and $\mu = 180°$, consequently in $w$ and $v$. For points on branch $w\,b\,v$ $\sin\mu$ is positive and therefore $\varphi$ decreases starting from $w$ towards $v$; for points on branch $v\,e\,w$ $\sin\mu$ is negative and consequently $\varphi$ increases from $v$ towards $w$ or reversally it decreases from $w$ towards $v$. As the *O. W. A.* of a liquid increases with decreasing values of $\varphi$, the property mentioned sub $2^0$ follows from this.

With the aid of fig. 2 the reader now may deduce several properties; briefly we shall discuss a single one.

We bring into osmotic contact $L_w$ with a liquid $L_q$.

$1^0$. when $L_q$ is situated within the region $W m w m'$, then water diffuses from $L_q$ to $L_w$; $L_w$ passes into an unsaturated liquid between $w$ and $W$.

$2^0$. when $L_q$ is situated on the osmotic curve $m\,w\,m'$, then nothing happens.

$3^0$. when $L_q$ is situated outside the region $W m w m'$, then water diffuses from $L_w$ to $L_q$; then $L_w$ separates solid $D$ and dries up totally or partially.

When a complex of $L_w$ and $L_i$ is represented f.i. by a point of $bD$, then we have the inversion:

$$\left(L_w \,\vdots\!\!\rightarrow L_i\right) \rightarrow \left(\text{solid } H \;\vdots\; L_b + \text{solid } H\right) \quad . \quad . \quad . \quad . \quad (23)$$

Here we have to mean by the *O.W.A.* of the ternary compound the

O.W.A. of the liquid $L_w$. Consequently curve $m w m'$ is the curve (O.W.A. $= D$). We now find:

1⁰. a ternary compound $D$, in osmotic contact with a liquid within the region $W m w m'$, removes water from this liquid, with formation of $L_w + D$ or an unsaturated solution between $w$ and $W$.

2⁰. a ternary compound $D$, in osmotic contact with a liquid out of the region $W m w m'$, does not remove water from this liquid.

Consequently when we bring into osmotic contact solid $D$ with a liquid $L_q$ (fig. 2) then water diffuses to the solid substance. When we bring into osmotic contact solid $D$ with one of the liquids $b$, $v$, $d$, $h$, $k$ or $i$, then nothing happens. When, however, we bring into osmotic contact one of those liquids with $L_w$, then $L_w$ is drying up totally or partially with separation of solid $D$.

Finally we still have to consider the occurrence of a binary compound between the components $X$ and $Y$. As, however, the results are in accordance with the now mentioned, we shall not discuss this case.

We have assumed with our considerations that water may diffuse from a liquid through a membrane towards other liquids and solid substances. Till now, we have supposed, however, that water can not diffuse through the membrane from solid hydrous substances (f. i. from the hydrate $H$ in fig. 1 or the hydrous compound $D$ in fig. 2). In many cases this is surely possible; we shall refer to this later.

When we assume this now, then some deductions must be changed in connection with the O.W.A. of the hydrate $H$ (and compound $D$).

Let us take the osmotic system

$$\left(H \,\vdots\, L\right) \quad \ldots\ldots\ldots\ldots \quad (24)$$

When a little water diffuses from $H$ to $L$ then $H$ passes into $L_v$ (fig. 1) with loss of water; on the left side of the membrane then arises $H + L_v$; consequently system (24) passes into:

$$\left(H + L_v \,\vdots\, L\right) \quad \ldots\ldots\ldots\ldots \quad (25)$$

Therefore, it now depends on the O.W.A. of $L_v$ with respect to that of $L$, which shall happen. When $L$ is situated in the region $v\,o\,X\,Y$ then $L$ has a greater O.W.A. than $L_v$; consequently water diffuses from $L_v$ to $L$. As $L_v$ should become unsaturated then, $H$ is dissolving, so that the quantity of $H$ decreases. When $H$ has totally disappeared, before $L$ has reached curve $ov$, then on the left side a liquid unsaturated and poor in water arises (viz. between $v$ and $Y$).

We have deduced from fig. 1: a hydrate $H$ in osmotic contact with a liquid $L$:

1⁰. removes water and flows away, when $L$ is situated within the region $W w m$.

$2^0$. rests unchanged, when $L$ is situated within the region $m\ X\ Y\ v\ d\ w$.

We now have to replace region $m\ X\ Y\ v\ d\ w$ in $2^0$. by the region $m\ o\ v\ d\ w$; in that case is also:

$3^0$. separates water and flows away when $L$ is situated within the region $v\ o\ X\ Y$.

Therefore we can assume that the hydrate $H$ has two different *O.W.A.*'s viz.

$1^0$. the *O.W.A.* of the solution $L_w$, saturated and rich in water, which arises when $H$ takes water.

$2^0$. the *O.W.A.* of the solution $L_v$, saturated and poor in water, which arises when $H$ loses water.

When it is necessary to distinguish the two *O.W.A.*, we shall call the second one the maximum or *M—O.W.A.*

We may also apply those considerations to a mixture of solid substances. In general we may say:

the *O.W.A.* of a solid substance or of a mixture of solid substances is that of the new system, which arises by taking water in;

the *M—O.W.A.* is that of the new system, which arises by losing water.

It is evident that only in that case there may be question of a *M—O.W.A.* when one or more of the solid substances contain water.

*Leiden, Lab. of Inorg. Chemistry.*

(*To be continued*).

## **Chemistry.** — *"Equilibria in systems, in which phases, separated by a semi-permeable membrane"* V. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of January 31, 1925).

### *Ternary equilibria with solid phases.*

After having discussed in the previous communications the occurrence of one solid phase, we now shall consider the case that several solid substances occur.

In fig. 1 *ac* represents the saturation-curve of $Y$, $b\,c$ that of $X$; the dotted curves *am*, *db* etc. are isotonic curves; with this is assumed that the $O.\,W.\,A.$ (osmotic water-attraction) of liquid $b$ is greater than that of $a$. Again the arrows indicate the direction, in which, in accordance with the deductions in previous communications, the $O.\,W.\,A.$ increases. Hence it appears that the $O.\,W.\,A.$ of the solution $c_1$ which is saturated with solid $X+Y$ is greater than that of all other unsaturated and saturated liquids. The $O.\,W.\,A.$ of $L_a$ is equal to that of $L_m$, that of $L_d$ equal to that of $L_b$, that of $L_e$ equal to that of $L_f$, etc.

We bring each of the liquids $a$, $b$ and $c$ in osmotic contact with an arbitrary liquid $L$. In accordance with the situation of $L$ we find the following.

1°. $L$ is situated within the region $W a m$. The $O.\,W.\,A.$ of each of the liquids $L_a$, $L_b$ and $L_c$ is greater than that of $L$; consequently water diffuses from $L$ towards the other liquids, which become unsaturated. Consequently we have the osmotic systems:

$$\left(L_a \underset{|}{\overset{|}{\leftarrow}} L\right) \;,\; \left(L_b \underset{|}{\overset{|}{\leftarrow}} L\right) \text{ and } \left(L_c \underset{|}{\overset{|}{\leftarrow}} L\right) \quad . \;.\; .\; . \tag{1}$$

in which the arrows indicate the direction in which the water is diffusing.

2°. $L$ is situated within the region $a\,m\,b\,d$. Now the systems are:

$$\left(L_a \underset{|}{\overset{|}{\rightarrow}} L\right) \;,\; \left(L_b \underset{|}{\overset{|}{\leftarrow}} L\right) \text{ and } \left(L_c \underset{|}{\overset{|}{\leftarrow}} L\right) \quad . \;.\; .\; . \tag{2}$$

Consequently water still diffuses from $L$ towards $L_b$ and $L_c$, but in contradistinction with sub 1°, from $L_a$ towards $L$.

3°. $L$ is situated within the region $b\,d\,c$. We now find:

$$\left(L_a \underset{|}{\overset{|}{\rightarrow}} L\right) \;,\; \left(L_b \underset{|}{\overset{|}{\rightarrow}} L\right) \text{ and } \left(L_c \underset{|}{\overset{|}{\leftarrow}} L\right) \quad . \;.\; .\; . \tag{3}$$

After the considerations in the previous communications the reader may easily deduce, which arises from the liquids $L_a$ $L_b$ $L_c$ and $L$, when osmotic equilibrium has established itself, whether solid substances will be separated or not, which those shall be, etc.

By the *O. W. A.* of a mixture $X + Y$ we mean the *O.W.A.* of the liquid, which is formed when we add some water to this mixture (see previous communications), consequently the *O. W. A.* of liquid *c*. As liquid *a* indicates the *O. W. A.* of $Y$ and liquid *b* that of $X$, it follows in connection with the discussed above:

the *O. W. A.* of a mixture of two solid components is greater than that of each of those components separately.

We now bring an arbitrary liquid $L$ into osmotic contact with the solid substances $X, Y$ and their mixture $X + Y$. We find the following.

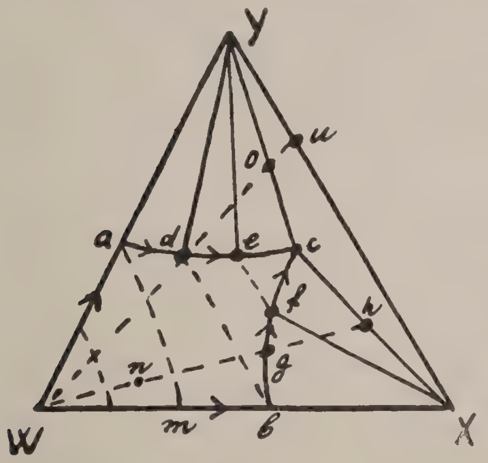

Fig. 1.

1⁰. $L$ is situated within the region *W a m*. The *O. W. A.* of $X$, $Y$ and $X + Y$ is greater than that of $L$; consequently water diffuses from $L$ towards the solid substances, which flow away totally or partially.

2⁰. $L$ is situated within the region *a m b d*. Now no water diffuses any more from $L$ towards $Y$; towards $X$ and the mixture $X + Y$ it does. The solid substance $X$ and the mixture $X + Y$, therefore, will still flow away totally or partially.

3⁰. $L$ is situated within the region *b d c*. Now still only water diffuses from $L$ towards the mixture $X + Y$, but no more towards $X$ nor towards $Y$.

Consequently the mixture $X + Y$ takes water in from all saturated and unsaturated solutions of the region *W a c b;* the component $X$ does so from the liquids of the region *W a d b* only and the component $Y$ only from the liquids of the region *W a m*.

As in the system $(X + Y + L_c \cdot \mid L_c + X + Y)$ the same liquid $L_c$ is at both sides of the membrane, of course osmotic equilibrium exists. When water diffuses from the left to the right, then the quantity of $X$ and $Y$ increases at the left side and decreases at the right side; this water-diffusion may continue either till the liquid $L_c$ at the left side, or till one of the solid substances disappears at the right side. As in this way an unlimited quantity of water (viz. defined only by the quantities of the several phases, but not by the character of the equilibrium) may diffuse from left to right, we may say that this diffusion is unlimited.

The water-diffusion in the inverse direction, viz. from the right towards the left, is unlimited also.

In the system $\left(X + L_c \mid L_c + X + Y\right)$ the water-diffusion from the left towards the right is unlimited also; then at the left side also the substance $Y$ is deposed. From right to left, however, this diffusion is not unlimited; because if water diffuses towards the left, then $L_c$ should change its composition along curve $c\,b$ starting from $c$ in the direction towards $b$ and get, therefore, a smaller *O.W.A.*; consequently the water taken in must diffuse backwards.

In the system $\left(X + L_c \mid L_c + Y\right)$ unlimited diffusion is possible in neither direction.

We now bring liquid $L_n$ (fig. 1) in osmotic contact with a solid mixture $X + Y$; the complex of this mixture is represented by point $u$. As the *O. W. A.* of $X + Y$ is equal to that of $L_c$, consequently water shall diffuse from $L_n$ towards $L_c$; $L_c$, however, rests unchanged as long as the two substances $X$ and $Y$ remain present. When the point $u$ has come on the line $Yc$ by access of water, then $X$ disappears. With further increase of water the liquid proceeds along the curve $cd$ and the straight line $dW$. As $L_n$ loses water, this liquid firstly proceeds along the line $n\,g$ and afterwards, with deposition of $X$ curve $g\,c$ till in $c$. Then the complex is represented by point $h$.

It now depends on the ratio, in which we bring together $L_n$ and the mixture $X + Y$, represented bij $u$, which osmotic equilibrium shall be formed at last. We imagine the complex of $L_n$ and $u$ to be represented by a point $K$ on the line $n\,u$ (not drawn). We now may distinguish several cases.

1$^0$. $K$ is situated on the line $n\,u$ within the triangle $h\,o\,u$.

It follows from the previous that the inversion:

$$\left(L_n \overset{|}{\underset{|}{\rightarrow}} X + Y\right) \rightarrow \left(X + L_c \mid L_c + X + Y\right)$$

occurs. Consequently $L_n$ proceeds along the straight line $n\,g$ and afterwards along curve $g\,c$ till in $c$.

2$^0$. $K$ is the point of intersection of the lines $n\,u$ and $h\,o$. We then get the inversion:

$$\left(L_n \overset{|}{\underset{|}{\rightarrow}} X + Y\right) \rightarrow \left(X + L_c \mid L_c + Y\right).$$

3$^0$. $K$ is situated on the line $n\,u$ further from $u$ than in the case, mentioned sub 2$^0$. Whe then may get f.i. the inversion:

$$\left(L_n \overset{|}{\underset{|}{\rightarrow}} X + Y\right) \rightarrow \left(X + L_f \mid L_e + Y\right).$$

When we represent the point of intersection of the lines *W u* and *Y e* by $s_1$ and that of the lines *W h* and *X f* by $s_2$, then the line $s_1\,s_2$ must go through *K*.

Of course it is possible also that the solid substance disappears at one or at both sides of the membrane, so that unsaturated solutions arise.

In fig. 2 we have assumed that, besides the two components *X* and *Y*, still also the hydrate *H* occurs as solid phase; *a d* is the saturation-curve of *H*, *d c* that of *Y* and *b c* that of *X*. The dotted curves are the isotonic curves; with this is assumed that the *O. W. A.* of $L_b$ is greater than that of $L_d$. Again the arrows indicate the direction in which the *O. W. A.* increases. It appears from the isotonic curves that the *O. W. A.* of $L_d$ is equal to that of $L_n$, that of $L_e$ equal to that of $L_b$ and that the *O. W. A.* of the liquid $L_c$, saturated with $X + Y$, is greater than that of all other unsaturated and saturated liquids.

It follows from our previous considerations that the *O. W. A.* of the solid substances *X*, *H* and the mixture $X + Y$ is equal to that of the liquids $L_b$, $L_a$ and $L_c$. We now still have to determine the *O. W. A.* of *Y*, that of $Y+H$ and the *M–O. W. A.* of *H* (see the previous communication).

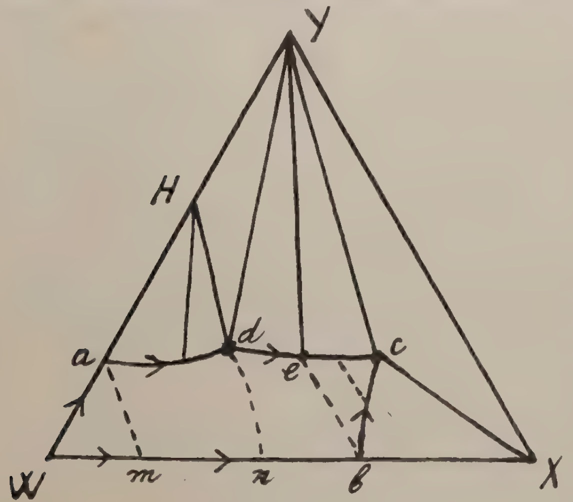

Fig. 2.

When we add a little water to the substance *Y*, then is formed an equivalent quantity of *H*; consequently the system $Y + H$ is formed. When we remove a little water from the hydrate *H*, then also the system $Y+H$ is formed. The *O. W. A.* of *Y* and the *M–O. W. A.* of *H* are, therefore, both equal to that of $Y+H$. In order to define the *O. W. A.* of $Y+H$, we consider the system

$$\left(Y+H \mid L\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As there is only one liquid, viz. $L_d$ (fig. 2) which may be in equilibrium with $Y + H$, the supposition is obvious that the *O. W. A.* of $Y + H$ shall be equal to that of $L_d$ and, therefore, also to that of the liquids of the isotonic curve *n d*.

We may confirm this in the following way. We represent the composition of:

$H$ by: $\beta \, Mol\, Y + (1-\beta)\, Mol\, W$
$L$ by: $x\, Mol\, X + y\, Mol\, Y + (1-x-y)\, Mol\, W.$

We take $m$, $n$ and $q$ quantities of $Y$, $H$ and $L$, each with the thermodynamical potential $\zeta_Y$ $\zeta_H$ and $\zeta$; we call $Z$ the total thermodynamical potential of the whole system (4). Consequently we have:

$$dZ = \zeta_Y\, dm + \zeta_H\, dn + \zeta\, dq + q \frac{\partial \zeta}{\partial x} dx + q \frac{\partial \zeta}{\partial y} dy \quad . \quad . \quad . \quad (5)$$

In equilibrium (4) the quantity of $Y$ rests constant at the left side of the membrane, also the quantities of $X$ and $Y$ at the right side and further the total quantity of water. Hence follow the conditions:

$$d\,(qx) = 0 \quad d\,(qy) = 0 \quad d\,(m + n\beta) = 0 \quad d\,[q + n\,(1-\beta)] = 0.$$

With the aid of those relations we may write instead of (5):

$$dZ = \left[\zeta_H - \beta\, \zeta_Y - (1-\beta)\left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y}\right)\right] dn \quad . \quad . \quad . \quad (6)$$

When we put:

$$\frac{\zeta_H - \beta\, \zeta_Y}{1-\beta} = \varphi_1 \quad \text{and} \quad \zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} = \varphi$$

then (6) passes into:

$$dZ = (1-\beta)\,(\varphi_1 - \varphi)\, dn \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It appears from the value of $\varphi$, that $\varphi$ determines the *O. W. A.* of the liquid $L$.

In order to find the meaning of $\varphi_1$ we consider the equilibrium $H + Y + L_d$ of fig. 2. When we represent the composition of $L_d$ by $x_1$ $y_1$ and $(1-x_1-y_1)$ then for this are true the equations:

$$\zeta_1 - x_1\frac{\partial \zeta_1}{\partial x_1} + (\beta - y_1)\frac{\partial \zeta_1}{\partial y_1} = \zeta_H \quad \text{and} \quad \zeta_1 - x_1\frac{\partial \zeta_1}{\partial x_1} + (1-y_1)\frac{\partial \zeta_1}{\partial y_1} = \zeta_Y\,.$$

We find from this:

$$\varphi_1 = \frac{\zeta_H - \beta\, \zeta_Y}{1-\beta} = \zeta_1 - x_1\frac{\partial \zeta_1}{\partial x_1} - y_1\frac{\partial \zeta_1}{\partial y_1}$$

so that $\varphi_1$ determines the *O. W. A.* of liquid $L_d$.

When system (4) is in equilibrium, then $dZ$ in (7) must be zero, consequently must be

$$\varphi = \varphi_1$$

or: the *O. W. A.* of $L$ must be equal to that of $L_d$; consequently $L$ must be situated on the isotonic curve $nd$, going through point $d$ (fig. 2). Consequently it follows from this:

the *O. W. A.* of the substance $Y$, that of the mixture $H + Y$ and the *M—O. W. A.* of the hydrate $H$ are equal to that of the liquid $L_d$, which is in equilibrium with $H + Y$.

When $L$ is situated in the region $Wnda$ (fig. 2) than is $\varphi > \varphi_1$. As only $dZ$ may be negative, $dn$ in (7) must, therefore, be positive. This means that the quantity $H$ in (4) increases, consequently, that water diffuses from the liquid towards the solid substances.

When $L$ is situated in the region $ndcb$ (fig. 2) then is $\varphi < \varphi_1$. Then it follows from (7) that $dn$ must be negative, consequently that in (4) water diffuses from the hydrate towards the liquid.

The region $Wadcb$ (fig. 2) is divided into four parts by the isotonic curves $am$, $dn$ and $be$. When we bear in mind that:

the $O.W.A.$ of $H$ is equal to that of the liquids of curve $am$,

the $O.W.A.$ of $H + Y$ and of $Y$ and the $M$—$O.W.A.$ of $H$ is equal to that of the liquids of curve $dn$,

the $O.W.A.$ of $X$ is equal to that of the liquids of curve $be$,

and the $O.W.A.$ of $X + Y$ is equal to that of the liquid $c$,

then we can easily deduce the following:

when we bring into osmotic contact a liquid $L$ with $H$, $H + Y$, $Y$, $X$ or $X + Y$ then:

1°. when $L$ is situated in the region $Wam$, water will diffuse from $L$ towards those substances;

2°. when $L$ is situated in the region $amnd$, $H$ will rest unchanged, but water shall diffuse from $L$ towards the other substances;

3°. when $L$ is situated in the field $dnbe$, water will diffuse from $H$ and from $H + Y$ towards $L$, $Y$ will rest unchanged and water shall diffuse from $L$ towards $X$ and $X + Y$;

4°. when $L$ is situated in the field $bec$, water shall diffuse from $H$ and from $H + Y$ towards $L$, $Y$ and $X$ shall rest unchanged and water shall diffuse towards $X + Y$.

It depends on the situation of the total complex, what will occur on both sides of the membrane, when the osmotic equilibrium is reached.

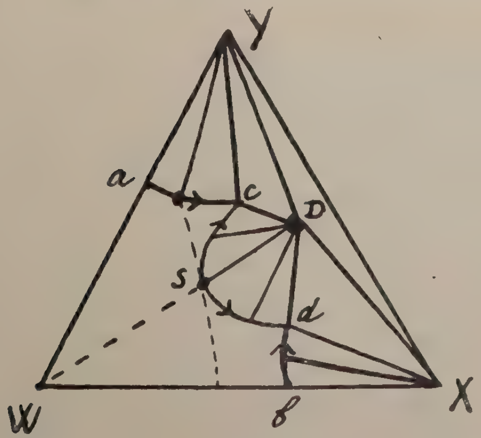

Fig. 3.

In figs. 3 and 4 we find, besides the saturation-curves of the two components, still also that of the ternary compound $D$. In fig. 3 the point of intersection $s$ of line $WD$ and curve $cd$ is situated on the stable part of the saturation-curve, in fig. 4 on the metastable part, which is not drawn. Consequently in fig. 3 $D$ is soluble without decomposition, in fig. 4 it is decomposed by water with separation of the substance $X$.

In accordance with our previous deductions, the *O.W.A.* increases in the direction of the arrows and is a minimum in point *s*.

The isotonic curve going in fig. 3 through point *s*, touches curve *csd* in this point; further we have assumed that the *O.W.A.* of liquid *s* is greater than that of *a*, but smaller than that of *b*.

We have assumed in fig. 4 that the *O.W.A.* of liquid *d* is smaller than that of *a*, of course it must be greater than that of *b*.

In fig. 3 the *O. W. A.* of the solid substances *X*, *Y* and *D* and that of the mixtures $X + D$ and $Y + D$ is equal to those of the liquids *b, a, s, d* and *c*; from this a.o. we may conclude the following:

when a ternary compound is soluble in water without decomposition, then the *O. W. A.* of *D* + one of the components is greater than that of *D* and of this component separately.

In fig. 4 the *O. W. A.* of *D* is no more equal to that of the liquid *s*, which is metastable now. When viz. we add some water to *D*, then the equilibrium $D + X + L_d$ is formed; consequently here the *O. W. A.* of *D* is equal to that of the liquid *d* and, therefore, also to that of $D + X$.

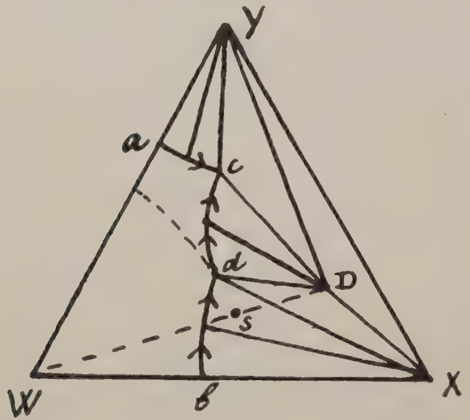

Fig. 4.

The reader now may easily deduce, which shall happen, when we bring into osmotic contact one or more solid substances with a liquid or when we bring into osmotic contact two liquids, saturated with solid substances or not.

We take into consideration an equilibrium $Q + R + L$ in which *Q* and *R* are solid substances. We imagine in a diagram the points *Q* and *R* united whith point *W*. When the point *L* is situated between the lines *W Q* and *W R* then we shall say that *L* is congruently saturated with the solid substances; when *L* is not situated between those lines, then we say that *L* is incongruently saturated.

Consequently in figs. 1 and 2 $L_c$ is congruently saturated with $X + Y$, in figs. 3 and 4 with $Y + D$; in fig. 3 $L_d$ is congruently saturated, in fig. 4 it is incongruently saturated with $X + D$; in fig. 2 $L_d$ is incongruently saturated with $H + Y$.

When a liquid consecutively proceeds along the stable parts of the different saturation-curves, f. i.: in fig. 1 the way *a c b* or *b c a*, then we shall say: the liquid proceeds along the saturation-curves. We now may deduce:

when a liquid proceeds along the saturation-curves, then its *O. W. A.*

changes from point to point; this becomes a maximum when the liquid is congruently saturated, a minimum in the point of solubility of a compound.

We see this proved in the figs. 1—4.

In figs. 1 and 2 the *O. W. A.* increases from *a* towards *c*, becomes a maximum here and decreases from *c* towards *b*, the same is also true for fig. 4.

In fig. 3 the *O. W. A.* increases from *a* till *c*, then it decreases from *c* till *s*, afterwards it increases from *s* till *d* and finally it decreases from *d* to *b*. In *c* and *d* the *O. W. A.* is a maximum, a minimum in *s*.

In the figs. 1—4 we have treated only some of the unnumbered ternary diagrams; with the aid of the considerations in this and the previous communications, the reader, however, will himself be able to examine easily the other cases.

*(To be continued).*

*Leiden, Lab. of Inorg. Chem.*

## **Physics.** — *"On the Structure of the Ultra-Violet Bands of Water Vapour."* By G. H. DIEKE. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of January 31, 1925).

The so-called ultra-violet emission bands of water vapour have been the subject of an extensive study [1]). They were formerly ascribed to the $H_2O$ molecule, or else to oxygen [2]). WATSON's [3]) researches, however, rendered it probable that the bands are due to the OH-molecule which is formed in the discharge tube or the flame. Also the structure of the bands pleads in favour of a di-atomic molecule.

After some investigators had arranged part of the lines in series, HEURLINGER [4]) succeeded in aranging almost all the lines of the band $\lambda$ 3064 in twelve branches, which he called $P_1^k$, $Q_1^k$, $R_1^k$, $P_2^k$, $Q_2^k$, $R_2^k$ $(k=1, 2)$. This band is the representative of a class of bands, which HEURLINGER calls "bands with doublet-series". A characteristic of this class is that the lines for small numbers in the series cannot be represented by DESLANDRES's formula.

The theoretical interpretation of the "$H_2O$"-bands, however, presented difficulties [5]). In contrast with many other bands there are here in one band no combination relations which allow us to isolate the terms. Recently the band $\lambda$ 2811 was measured by WATSON [3]), who succeeded in showing that its structure is perfectly analogous to the structure of the band $\lambda$ 3064, and that the two bands must belong to the same final state. WATSON found again that the lines themselves do not satisfy the simple theory of band spectra, but that this is more or less the case with the doublet middles.

When use is made of WATSON's measurements, and these are combined with those of GREBE and HOLTZ [6]) of the band $\lambda$ 3064, it appears possible to get a full insight into the formal structure of these bands without it being necessary to make any supposition concerning the structure of the molecule emitting the bands. The values of all the rotational terms besides a constant — can be calculated, and from the course of the rotational energy as a function of the quantum number $m$ conclusions can then be drawn concerning the structure of the molecule. In this communication, however, only the formal structure of the bands will be derived and we will not enter into the structure of terms themselves and the conclusions that may be drawn from them.

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[1]) Earlier literature in KAYSER, Handbuch der Spectroscopie, Bd. V.

[2]) W. STEUBING, Ann. d. Phys. **33**, p. 553, 1910; **39**, p. 1408, 1912. A. REISS, ZS. f. phys. Chemie **88**, p. 513, 1914.

[3]) W. W. WATSON, Astroph. Journal **60**, p. 145, 1924.

[4]) T. HEURLINGER, Untersuchungen über die Struktur der Bandenspektra, Lund, 1918.

[5]) Compare A. SOMMERFELD, Atombau und Spektrallinien, 3rd impr., p. 527.

[6]) L. GREBE und O. HOLTZ, Ann. d. Phys. **39**, p. 1243, 1912.

TABLE I.

| $m$ | $Q_1^1(m) - P_1^1(m+1)$ | | $R_1^1(m) - Q_1^1(m+1)$ | | $Q_2^1(m) - P_2^1(m+1)$ | | $R_2^1(m) - Q_2^1(m+1)$ | |
|---|---|---|---|---|---|---|---|---|
| | λ 3064 | λ 2811 | λ 3064 | λ 2811 | λ 3064 | λ 2811 | λ 3064 | λ 2811 |
| 2 | 61.36 | 61.02** | 60.94* | 61.01 | 83.61* | 83.52* | 83.74 | 83.88 |
| 3 | 101.48* | 101.41 | 101.11* | 101.05 | 117.77 | 117.90 | 118.50 | 118.40 |
| 4 | 140.68* | 140.49 | 140.29 | 140.14* | 152.91 | 152.60 | 153.97 | 153.76 |
| 5 | 178.81 | 178.87 | 178.78 | 178.66* | 187.73 | 187.66 | 189.62 | 189.68 |
| 6 | 216.19 | 216.46* | 216.58 | 216.89 | 222.70 | 222.74 | 225.64 | 225.18** |
| 7 | 253.13* | 253.11 | 253.91 | 254.26* | 257.37* | 257.76* | 261.57* | 262.02* |
| 8 | 288.96* | 289.18 | 290.84 | 290.43** | 292.15** | 292.23 | 297.47* | 297.66 |
| 9 | 324.53 | 324.89* | 327.30* | 327.23 | 326.42 | 326.58 | 333.28* | 333.52* |
| 10 | 359.38* | 359.51 | 363.22 | 363.07* | 360.20 | 360.37* | 368.87* | 368.81 |
| 11 | 393.75 | 393.76 | 398.67 | 398.92 | 393.87 | 394.01* | 404.10* | 404.16 |
| 12 | 427.35 | 426.72 | 433.87* | 433.78 | 426.88 | 427.22 | 439.30* | 439.38* |
| 13 | 460.41 | 460.27* | 468.24 | 468.87* | 459.38 | 459.20* | 473.24 | 473.45 |
| 14 | 492.78 | 493.05 | 502.14 | 502.32 | 491.40 | 491.65 | 507.17 | 506.81* |
| 15 | 524.46 | 525.21 | 535.76* | 535.90 | 522.61 | 522.90 | 540.48* | 540.78 |
| 16 | 555.43* | 555.44 | 568.27 | 568.69 | 553.18 | 553.33 | 573.25 | 573.35 |
| 17 | 585.92 | 585.85 | 600.34 | 600.65* | 583.30 | 583.16 | 605.43 | 606.00* |
| 18 | 615.54 | 615.40* | 631.80 | 632.48* | 612.68 | 612.31 | 636.80 | 637.26 |
| 19 | 644.24 | 644.15* | 662.76 | 663.38* | 640.99 | 640.77 | 667.02 | 668.16 |
| 20 | 672.08 | 671.73* | 692.70* | — | 668.70 | 668.25 | 697.73 | — |
| 21 | 699.20* | 699.62* | 722.17 | — | 695.28 | 695.92* | 727.13 | — |

| $m$ | $Q_1^2(m) - P_1^2(m+1)$ | | $R_1^2(m) - Q_1^2(m+1)$ | | $Q_2^2(m) - P_2^2(m+1)$ | | $R_2^2(m) - Q_2^2(m+1)$ | |
|---|---|---|---|---|---|---|---|---|
| | λ 3064 | λ 2811 | λ 3064 | λ 2811 | λ 3064 | λ 2811 | λ 3064 | λ 2811 |
| 2 | — | 58.96 | — | — | 80.50* | 80.58 | — | — |
| 3 | 97.04* | 98.17* | — | — | 111.09* | 114.07* | — | — |
| 4 | 135.37* | 135.08 | — | 134.51 | 147.14 | 146.48** | — | 140.20**? |
| 5 | 171.94 | 172.05 | 171.92 | 172.06 | 180.96 | 180.74 | — | 180.68*? |
| 6 | 208.09 | 207.68 | 208.33* | 207.77** | 214.34 | 213.80** | 216.78 | 217.08 |
| 7 | 243.29* | 243.74* | 243.75 | 243.68* | 247.72 | 247.53 | 251.49 | 252.97** |
| 8 | 277.82 | 277.96* | 279.48 | 280.05** | 280.72 | 280.84 | 285.62 | 286.34** |
| 9 | 311.96 | 311.15* | 314.24 | — | 314.54* | 313.74 | 320.14 | — |
| 10 | 345.48 | 344.94* | 384.73 | — | 346.66 | 346.93* | 354.73 | — |
| 11 | 378.57 | 378.21 | 382.77 | — | 378.69 | — | 389.52 | — |

I. The differences:

$$Q_i^1(m) - P_i^1(m+1) \qquad \text{and} \qquad R_i^1(m) - Q_i^1(m+1)$$

have within the limits of the errors of observation the same value in λ 3064 and λ 2811. (Cf. table I [1]), i. e. $Q_i^1(m)$, $P_i^1(m+1)$ and $R_i^1(m+1)$ must have the same initial state, which we call $F_i^1(m)$ [2]). ($F_i^1(m)$ = energy divided by $h$). We may, therefore, write:

$$\left.\begin{aligned} P_i^1(m) &= F_i^1(m-1) - f_i^P(m) \\ Q_i^1(m) &= F_i^1(m) \qquad\;\; - f_i^Q(m) \\ R_i^1(m) &= F_i^1(m+1) - f_i^R(m) \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (1)$$

From the fact that

$$Q_i(m) - P_i(m+1) \neq R_i(m) - Q_i(m+1)$$

follows that the equation

$$f_i^P(m) = f_i^Q(m) = f_i^R(m)$$

which is satisfied in a normal band, *cannot* be valid here.

Analogous relations hold for the branches $P_1^2$, $Q_i^2$, $R_i^2$ [3]).

II. The six branches $P_i^1$, $Q_i^1$, $R_i^1$ ($i = 4, 2$) form one band (which we shall call I), and the six branches $P_i^2$, $Q_i^2$, $R_i^2$ another one (II), belonging to another oscillation jump. If, therefore, we ascribe the band λ 3064 I to the oscillation transition $n_1 \rightarrow n_2$, we obtain the following scheme for the oscillation jumps of the other bands [4]).

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[1] In the tables * denotes that one, ** that more than one of the lines, from which the differences have been calculated, coincide with other lines.

[2] When judging about the agreement, it should be borne in mind that no importance should be attached to the second decimal. Nor is it impossible that the presence of satellites has affected the accuracy of the measurements.

[3] The lines of the branch λ 3064 II $R_2$, which could not be classified by HEURLINGER, are given by FORTRAT (Journal de phys. **5**, p. 20, 1924) according to his new measurements. They do not, however, fit into any of the combination relations following from the structure given here. FORTRAT himself already pointed out that the relation $R_1 - R_2 = P_1 - P_2 - \delta$ expected by HEURLINGER, is not fulfilled.

If FORTRAT's lines are, however, arranged in the reversed order, then they satisfy all the combination relations within the limits of the errors of observation. For the calculation of the values in the tables I and II this arrangement has been chosen.

It appears from the values with a ? in the tables that the lines λ = 2876,336 and λ = 2875.500 in the band λ 2811 cannot be considered as $R_2^2(4)$ and $R_2^2(5)$.

[4] On the assumption that $n_1 = n_2 = 0$ which is the most probable one the oscillation constants can be calculated from the provisional position of the zero lines. If the oscillation energy according to KRATZER is written $hn\nu^0(1-nx)$, one gets

$$\nu_1^0 = 3085.4; \qquad \nu_1^0 x_1 = 97.4; \qquad \nu_2^0(1-x_2) = 3569.8.$$

$$\begin{array}{lcc} & \text{I.} & \text{II.} \\ \lambda\, 3064 & n_1 \rightarrow n_2 & n_1+1 \rightarrow n_2+1 \\ \lambda\, 2811 & n_1+1 \rightarrow n_2 & n_1+2 \rightarrow n_2+1 \end{array} \quad \ldots\ldots \quad (2)$$

That the pieces called I and II of what is called usually a band are in reality two different bands with different oscillation jumps is rendered probable by the fact that the quotient of the term differences in I and II is independent of *m*, which is an indication that only the constant *B*, which contains the moment of inertia, is different in the term formulae. A direct confirmation of this is obtained with the aid of the combination relations. According to the above scheme λ 3064 II and λ 2811 I must have the same initial state. Apart from small irregular deviations which must be attributed to errors of observation the differences $R_i^2(m)-P_i^2(m)$ in λ 3064 and $R_i^1(m)-P_i^1(m)$ in λ 2811 now appear actually to have the same values (table II 5th—7th columns). This confirms, therefore, the scheme of the oscillation transitions, and proves at the same time that:

$$f_i^P(m) = f_i^R(m) = f_i(m).$$

III. When the upper indices are omitted and $f_i'$ is written instead of $f_i^Q$, the six branches of a band are represented by:

$$\begin{array}{ll} P_1(m) = F_1(m-1) - f_1(m) & P_2(m) = F_2(m-1) - f_2(m) \\ Q_1(m) = F_1(m) \quad\;\; - f_1'(m) & Q_2(m) = F_2(m) \quad\;\; - f_2'(m) \\ R_1(m) = F_1(m+1) - f_1(m) & Q_2(m) = F_2(m+1) - f_2(m) \end{array} \quad . \quad (3)$$

Now the term-differences, and with them the relative values of the terms can all be calculated. One gets

$$\Delta F_i(m-1) = F_i(m+1) - F_i(m-1) = R_i(m) - P_i(m)$$

$$\Delta f_i(m) = f_i(m+2) - f_i(m) = R_i\ (m) \quad - P_i(m+2) \qquad (i=1,2)$$

$$\Delta f_i'(m) = f_i'(m+2) - f_i'(m) = R_i(m+1) - Q_i(m+2) + Q_i(m) - P_i(m+1)$$

These values are given in the tables II and III.

HEURLINGER already observed that $R_1(m) - P_1(m)$ and $R_2(m) - P_2(m)$ differ by a small, about constant amount. This means that the difference between $F_1(m)$ and $F_2(m)$ will increase slowly and almost linearly with *m*. It is further seen from the tables that the difference between $f_i(m)$ and $f_i'(m)$ increases with $m^2$, and this may be interpreted as a small difference in the moments of inertia of the molecules in the conditions $f_i(m)$ and $f_i'(m)$.

On the other hand the values of $f_1$ and $f_2$ show comparatively great differences for small *m*; they approach each other more and more with increasing *m*, which indicates that $f_1$ and $f_2$ belong to a different direction of rotation.

The interpretation of the other properties of the terms would necessitate a further discussion of the structure of the molecule, and will therefore be omitted in this communication.

The analogy with the $(C+H)$-band $\lambda$ 3900, to which HEURLINGER already drew the attention, is corroborated by the combination relations. The same scheme (3) which applies to the bands considered here, was

TABLE II.

| $m$ | $\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 3064 I | $\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 3064 I | $\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 3064 II | $\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 3064 II | $\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 2811 I | $\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 2811 I | $\Delta F_1(m-1)$ $R_1(m)-P_1(m)$ $\lambda$ 2811 II | $\Delta F_2(m-1)$ $R_2(m)-P_2(m)$ $\lambda$ 2811 II |
|---|---|---|---|---|---|---|---|---|
| 2 | 101.44 | 101.39 | — | — | 96.66* | 96.74 | — | — |
| 3 | 168.94 | 169.48 | — | — | 160.75* | 160.88 | — | — |
| 4 | 236.35 | 236.99 | — | — | 224.60* | 225.02 | 213.51* | 205.82** ? |
| 5 | 303.69 | 304.08 | 288.87 | — | 288.47 | 288.90 | 273.73 | 271.92** ? |
| 6 | 370.16 | 370.70 | 352.20 | 352.18 | 352.02 | 351.95* | 333.71* | 333.75 |
| 7 | 436.10 | 436.78 | 414.44 | 414.84 | 414.90* | 415.50* | 392.44 | 394.48** |
| 8 | 501.80* | 501.90** | 476.85 | 476.96 | 476.59* | 477.37 | 451.51* | 451.80* |
| 9 | 566.27* | 566.81** | 537.90 | 537.79 | 538.04 | 538.60 | — | — |
| 10 | 630.26 | 630.69* | 598.47 | 599.11 | 598.45* | 599.12 | — | — |
| 11 | 693.15 | 693.48* | 658.05 | 659.75 | 658.51 | 658.89 | — | — |
| 12 | 755.30* | 755.94* | 717.13 | 717.42 | 717.05 | 717.90** | — | — |
| 13 | 815.97 | 816.40 | 774.69 | — | 774.49* | 775.27 | — | — |
| 14 | 875.65 | 876.15 | 832.66 | — | 830.72* | 830.60** | — | — |
| 15 | 934.09 | 934.50* | — | — | 886.42* | 886.92 | — | — |
| 16 | 991.03 | 991.53 | — | — | 940.70* | 940.41 | — | — |
| 17 | 1046.81 | 1047.25 | — | — | 992.13 | 992.85* | — | — |
| 18 | 1100.84 | 1101.27 | — | — | 1043.13 | 1043.26 | — | — |
| 19 | 1153.46 | 1153.25 | — | — | 1092.22 | 1092.39 | — | — |
| 20 | 1204.26 | 1204.61 | — | — | — | — | — | — |
| 21 | 1253.42 | 1253.71 | — | — | — | — | — | — |
| 22 | 1300.49 | 1300.87 | — | — | — | — | — | — |
| 23 | 1346.43 | — | — | — | — | — | — | — |
| 24 | 1389.58* | — | — | — | — | — | — | — |
| 25 | 1431.01 | — | — | — | — | — | — | — |

TABLE III.

| $m$ | $\Delta f_1(m)$ $R_1(m) - P_1(m+2)$ | | $\Delta f_2(m)$ $R_2(m) - P_2(m+2)$ | | $\Delta f_1'(m)$ $Q_1(m) - P_1(m+1) +$ $R_1(m+1) - Q_1(m+2)$ | | $\Delta f_2'(m)$ $Q_2(m) - P_2(m+1) +$ $R_2(m+1) - Q_2(m+2)$ | |
|---|---|---|---|---|---|---|---|---|
| | λ 3064 I | λ 2811 I | λ 3064 I | λ 2811 I | λ 3064 I | λ 2811 I | λ 3064 I | λ 2811 I |
| 2 | 162.42 | 162.42 | 201.51 | 201.78 | 162.47* | 162.07** | 201.11 | 201.92* |
| 3 | 241.79 | 241.54 | 271.47 | 271.00 | 241.77* | 241.55* | 271.74 | 271.66 |
| 4 | 319.10 | 319.01* | 341.70 | 341.48 | 319.46* | 319.15* | 342.53 | 342.28 |
| 5 | 394.97 | 395.12 | 412.32 | 412.42 | 395.39 | 395.76 | 413.27 | 412.84** |
| 6 | 469.71* | 470.00 | 483.01 | 482.94* | 470.10 | 470.72** | 484.27* | 484.76* |
| 7 | 542.87* | 543.44* | 553.72 | 554.25* | 543.97* | 543.54** | 554.84** | 555.42* |
| 8 | 615.37 | 615.32* | 623.89** | 624.24 | 616.26** | 616.41 | 625.43** | 625.75* |
| 9 | 686.68 | 686.74 | 693.48** | 693.89 | 687.75 | 687.96** | 695.29* | 695.39 |
| 10 | 756.97 | 756.83* | 762.74* | 762.82* | 758.05* | 758.43 | 764.30* | 764.53* |
| 11 | 826.02 | 825.71 | 830.98* | 831.38 | 827.62* | 827.54 | 833.17* | 833.39** |
| 12 | 894.28* | 894.05* | 898.68* | 898.58** | 895.59 | 895.59* | 900.12 | 900.67 |
| 13 | 961.02 | 961.92** | 964.64 | 965.10 | 962.55 | 962.59* | 966.55 | 966.01** |
| 14 | 1026.60 | 1027.53* | 1029.78 | 1029.71* | 1028.54* | 1028.95* | 1031.88* | 1032.13 |
| 15 | 1091.19 | 1091.34 | 1093.66* | 1094.11 | 1092.73 | 1093.90* | 1095.86 | 1096.25 |
| 16 | 1154.19 | 1154.54 | 1156.55 | 1156.51 | 1155.77* | 1156.09* | 1158.61 | 1158.33* |
| 17 | 1215.88 | 1216.05 | 1218.11 | 1218.31* | 1217.72 | 1218.33* | 1220.10 | 1220.42 |
| 18 | 1276.04 | 1276.63 | 1277.79 | 1278.03 | 1278.30 | 1278.78** | 1279.70 | 1280.47 |
| 19 | 1334.84 | 1335.11 | 1335.72 | 1336.41 | 1336.94* | — | 1338.72 | — |
| 20 | 1391.90 | — | 1393.31 | — | 1394.25 | — | 1395.83 | — |
| 21 | 1447.57 | — | 1448.68 | — | 1449.44* | — | 1450.83 | — |
| 22 | 1501.25* | — | 1502.35 | — | 1503.67 | — | — | — |
| 23 | 1553.77 | — | — | — | 1555.69* | — | — | — |
| 24 | 1603.77 | — | — | — | 1606.09 | — | — | — |

found for the $(C+H)$-band by KRATZER[1]). The analogy, however, does not hold for the structure of the terms themselves, which cannot be represented here by KRAMERS and PAULI's formula or by its extension given by KRATZER.

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[1]) A. KRATZER, ZS. f. Phys. **23**, p. 298, 1924.

In the $(C+H)$-band $\lambda$ 3900 KRATZER assumed terms $F'_i$ in $Q_i$, which might differ somewhat from $F_i$. The presence of such terms in the "watervapour bands" is not excluded. No certainty can, however, be obtained on this head from the available observations.

*Satellites.*

HEURLINGER found that some lines are accompanied by satellites, and FORTRAT [1]) proved by new measurements that the presence of satellites is no exception, but the rule in most of the branches. The presence of these satellites may be due to other combinations between the same terms as are also responsible for the main lines. The available measurements, however, do not enable us to come to a positive decision, and it is very well possible that there are still other terms differing little from those found already. Especially in the $Q$-branches the matter is very complicated on account of the presence of satellites. If it is tried to use for the derivation only the terms found, $Q_2$ with its three satellites is e.g. represented by (from red to violet):

$$F_1(m) - f'_2(m); \quad \underline{F_2(m) - f'_2(m)}; \quad F_1(m) - f_2(m); \quad F_2(m) - f_2(m).$$

For not too small $m$ the last satellite must, however, be further distant from the main line than was observed by FORTRAT, and if the accuracy of the measurements has not been vitiated by the concurrence of several faint lines, this would suggest the presence of another term which may be identical with $F'_i$ (cf. p. 177). For so far as the accuracy of the measurements admits of a judgment, the satellites of $P_1$ and $R_2$ are quantitatively represented by:

$$\sigma P_1 = F_2(m-1) - f_1(m); \qquad \sigma R_2 = F_1(m+1) - f_2(m).$$

More extensive measurements of the satellites, also in the band $\lambda$ 2811 will without doubt be able to give information about those particulars of the fine structure of the $O+H$-bands, about which so far no certain decision was possible.

Perhaps the circumstance that the "$H_2O$"-bands were observed by WOOD and his collaborators [2]) in fluorescence, may offer a possibility of arriving at a definite decision by which molecule these bands are emitted. The said investigators found that in nitrogen contaminated by watervapour the "$H_2O$"-bands appear in fluorescence, but not in dry nitrogen, not when it is contaminated by oxygen either. If WATSON's view, that the bands must be ascribed to the $OH$-molecule, is correct, the appearance of the bands in fluorescence would have to be explained in this way that excited $N_2$ molecules, through impacts of the second kind, dissociate an $H_2O$-molecule into an excited (or ionized) $OH$-molecule and an $H$-atom. If so this is not a case of true fluorescence, and in pure sufficiently diluted water-vapour, where impacts of the second kind cannot take place, the fluorescence would, accordingly, have to disappear, whereas it would have to continue to exist if it was due to the $H_2O$-molecules.

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[1]) R. FORTRAT, Journal de phys. **5**, p. 20, 1924.

[2]) R. W. WOOD, Phil. Mag. 20, p. 707, 1910.
R. W. WOOD and G. A. HEMSALECH, Phil. Mag. 27, p. 899, 1914.
C. F. MEYER and R. W. WOOD, Phil. Mag. 30, p. 449, 1915.

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## **Botany.** — "*Conditions influencing the production of colouring matter of Monascus purpureus* WENT". By Prof. SHIN-ICHI HIBINO. (Communiated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of March 28, 1924).

Up to the present time, a large number of bacteria and fungi which produce special colouring matter have been described.[*] Among these organisms, however, those which have been investigated as to the physiology of the production of colouring matter are very limited in number.

*Monascus purpureus* WENT, which was first described and investigated in detail by WENT (20), is known as producing a characteristic red colouring matter, the chemical nature of which was examined by PRINSEN GEERLIGS (14), who considered it to be an anthraquinon derivative and by BOORSMA (2), who isolated the $\alpha$- and $\beta$-oryzaerubin components. However, no investigation on the conditions influencing the production of colouring matter has been previously done, and its chemical construction is quite unknown, also.

In former research, special attention was paid to the action of magnesium in the culture medium, for Mg must be considered an essential element for the production of colouring matter in bacteria (THUMM (18), KUNZE (8), BENECKE (1), and SAMKOW (15)), and in fungi (KOSSOWICZ (7), MEDISCH (10) and NAUMANN (13)). In addition to Mg, the importance of phosphorus and sulphur in this respect, was also noticed by some of these investigators, especially by GESSARD (4) and JORDAN (6), who maintained that the essential elements are P and S and that Mg was not essential for the pigment bacteria.

The effect of the sources of nitrogen and carbon and other physical conditions relating to the production of the colouring matter of these organisms were also observed by the above mentioned investigators, as well as by MILBURN (11), SCHKORBATOW (16), SELIBER (17), and others.

So far in the investigations on the production of colouring matter by fungi or bacteria, nothing has been done to compare the quantitative relation between growth and the production of colouring matter although this has great importance in the metabolic physiology of the organisms because of the close connection of the two functions.

In this preliminary note a report is given of the present research, in which this relation was observed, as well as a remarkable effect of Mg, which acts as a stimulant, the effect of carbohydrates as a source of carbon, and other conditions dealing with the production of colouring matter of *Monascus purpureus*; the investigation having been done on material cultured in the Botanical Laboratory in Utrecht.

### General description of methods.

As to the methods generally used, special attention is drawn to the following:

Glassware. For all the cultures, Jena-glass ERLENMEYER flasks were used. These were previously boiled with 15 % hydrochloric acid for half an hour, then washed carefully with distilled water, prepared by the following method:

Water. Water which was used in the preparation of the culture media and for washing glass-ware was distilled in a Jena-glass still.

Chemicals. "Chemically pure" chemicals were used. Inorganic chemicals were always recrystallized twice or thrice and in each case even the slightest trace of Mg, $SO_4$, and $PO_4$, which should be absent in the present experiment, was shown microchemically by the reaction of Mg mixture, $BaCl_2$, and Ammonium molybdate mixture.

LINTNER's soluble starch (which I myself made with great care), saccharose, maltose, dextrose, galactose, and lactose showed almost no trace of these three minerals. Fructose, glycogen, inulin, and dextrine, which are naturally very difficult to purify, showed a slight degree of impurity and were used without recrystallization.

Cotton stoppers. Special attention was paid to the cotton stoppers, as I realized that during sterilization they give some mineral impurity to the media, therefore the cotton was boiled in 2 % HCl, washed with distilled water, and dried.

Sterilization. Media were sterilized in the autoclave, under two atmospheres, for half an hour, the subsequent loss of water being corrected by the addition of sterilized water.

Inoculation. As *Monascus* produces its spores in the culture medium itself and the mycelium mass is very compact, it is not easy to get spores. Therefore the fungus mass on the surface of a new and vigorous normal culture was cut into fine pieces of as nearly similar size as possible and brought into a flask containing a certain amount of distilled water at 30° C., where they were soaked for one hour to purify them of any substance present. Each piece was then used for inoculation.

Temperature. All experiments were carried out in a room of constant temperature of 27° C., the temperature most suitable for this fungus.

Determination of dry weight of fungus body. When all other observations had been made, each mass of fungus was isolated from the medium, was carefully washed in water of 45° C., dried at 105° C., and the constant weight determined.

Determination of colour intensity. AUTENREATH's colorimeter was used. It is, however, difficult to make the determination accurately, as the purification of the colouring matter of this fungus is not yet possible, for it is really a mixture of various colouring matter, as I shall explain later. Therefore I have taken as standard, in a scale 0—1000, the solution from the maltose culture in which this fungus constantly produced the most intense colour. By this means we can make a relative comparison of the intensity of colour, being supplemented afterwards by the qualitative description. In the present investigation, only the water soluble colouring matter was quantitatively observed, the insoluble part being described only qualitatively.

Effects of the essential anions and cations in the culture media upon the production of colouring matter.

The normal culture medium consisted of 3 parts of mineral substances in molecular concentration, $N/20\ KNO_3$, $N/100\ KH_2PO_4$, and $N/200\ MgSO_4$ with 3⁰/₀ of soluble starch, and was found to be very suitable for *Monascus*.

In order to investigate the special action of these two anions, Mg and K, and three cations, $-H_2PO_4$, $=SO_4$, and $-NO_3$, thirteen groups of culture media were prepared. Each contained the essential anions and cations in the molecular concentration, with the exception of one anion or cation, which, being omitted, was replaced by other salts ("free culture"), or, a certain small amount was added ("trace culture"). In all cases the total concentration or the media was always isomolecular.

Each ERLENMEYER flask (300 cc.) contained 150 cc. of the medium and 0.5 cc. of $N/5$ citric acid, with one exception ("normal alkaline"). After ten weeks of cultivation, the following results were observed:

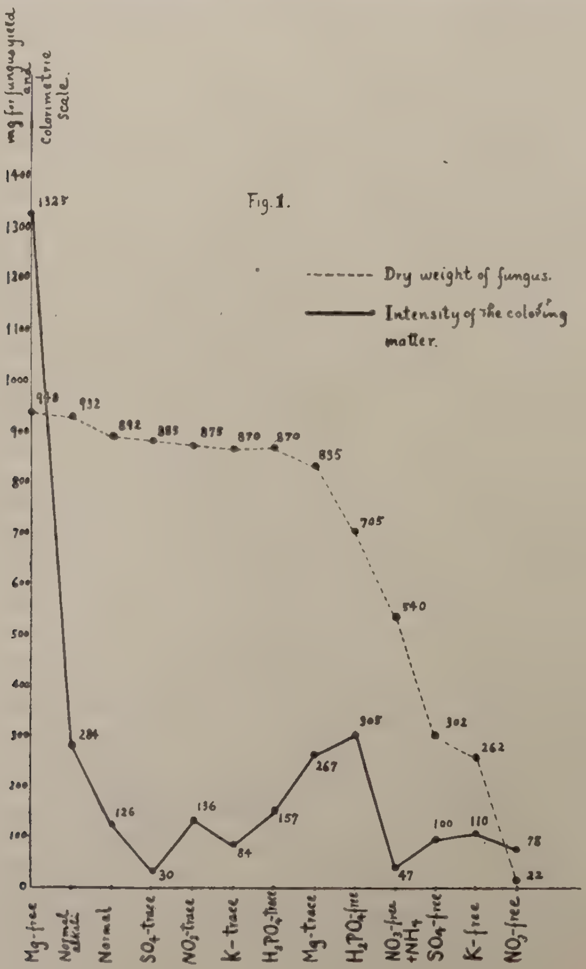

Fig. 1.

The relation between the production of colouring matter and the essential elements was naturally not similar to that between fungus growth and the essential elements.

Fungus growth was almost normal in the case of the following media: "normal alkaline", "$SO_4$ trace", "$NO_3$ trace", „$H_2PO_4$ trace", and „Mg trace". It was hindered in "$H_2PO_4$ free", and "$NH_4$ free", still further hindered in "$SO_4$ free", and "K free", and almost checked in "$NO_3$ free", as N is needed by the fungus in rather large amounts for plastic substance.

As to the production of colouring matter in the "$NO_3$ trace", "K trace", and "$H_2PO_4$ trace" cultures, and in the "$SO_4$ free", "K free", and "$NO_3$ free" cultures, the intensity produced was almost similar to the normal culture. It was a little stronger in the "normal alkaline", "Mg trace", and $PO_4$ trace" cultures.

As the source of nitrogen for the growth of the fungus and the production of colouring matter, $NH_4$ is less favourable than $NO_3$.

In the "$SO_4$ free" culture, the colour of the medium became yellowish.

In general, the mineral constituents of the culture media influence the tone of the colour produced.

It is remarkable that the fungus very intensively produced colouring matter in the "Mg free" culture, while the fungus yield was just the same as in the normal and "Mg trace" cultures. This curious fact causes one to consider that there was still present some small amount of Mg due to the impurity of the chemicals, which were purified, however, with considerable care. This possibility was ascertained by the following experiment.

### Influence of the various concentrations of Mg.

Culture media containing 0.5 $^0/_0$ $KNO_3$, 0.1 $^0/_0$ $KH_2PO_4$, and 3 $^0/_0$ soluble starch or maltose, to which various amounts of $MgSO_4$ in molecular concentration were added, were inoculated and the results summarized. See fig. 2.

When the Mg concentration was decreased from $\frac{1}{2} N$ to $\frac{1}{100,000} N$, the fungus yield showed almost no difference: the production of colouring matter, however, gradually increased in the descending series, suddenly becoming remarkably intensive in $\frac{1}{100,000} N$, but when the Mg concentration is decreased to an infinitesimal degree, neither fungus yield nor production of colouring matter occurred.

In order to leave Mg out of the media absolutely, more careful purification of the chemicals and glass-ware was undertaken, and in addition to the Jena-glass flasks, quartz flasks were used. Under such conditions, a light yield of fungus and a slight production of colouring matter still occurred, while the almost colourless medium showed a light brown tinge. This result assures one that Mg acts as a stimulant in the production of colouring matter of this fungus; one may say it acts almost oligodynamically. It also seems probable that Mg is not a component of this colouring matter and that, although Mg is of course an essential element

(MOLISCH (12), BENECKE (1), LOEW (9), GÜNTHER (5), and others), a certain small quantity is quite sufficient for the growth of the fungus.

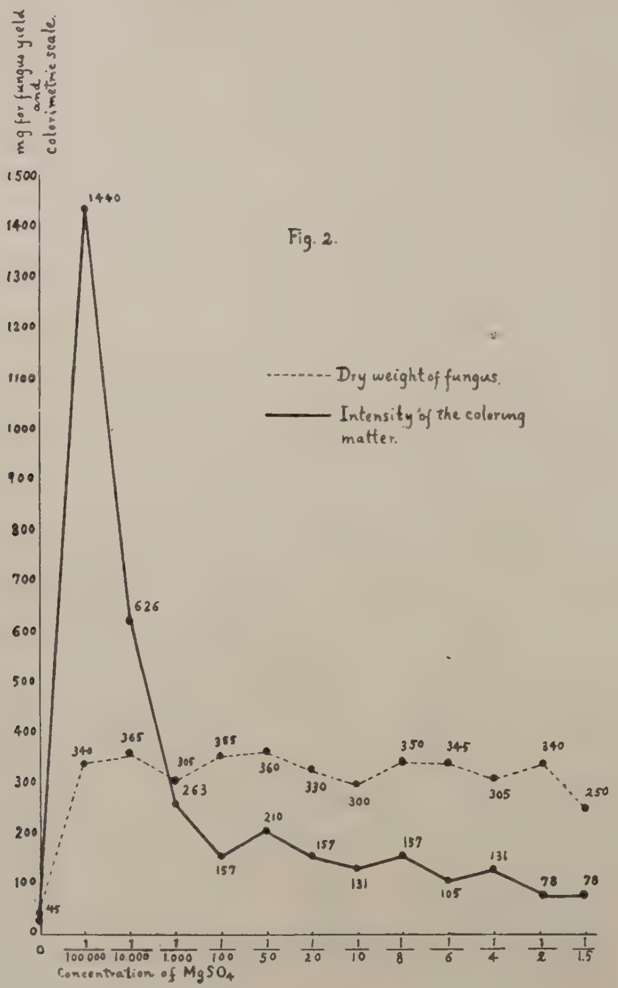

Fig. 2.

### Influence of the carbohydrates.

The influence of the carbohydrates, which provide the source of carbon in assimilation and for the production of colouring matter, was investigated. Thirteen sets of culture media were prepared, in which the mineral parts consisted of 0.5 °/₀ $KNO_3$, 0.1 °/₀ $KH_2PO_4$, and 0.01 °/₀ $Mg\,SO_4$ and to which various carbohydrates were added in three different molecular concentrations, as follows:

Concentration I. *N*/2 for hexoses and polysaccharides and *N*/4 for disaccharides, the concentration of which is isomolecular to *N*/2 hexose, when they are completely hydrolized by the fungus enzyme.

Concentraion II. *N*/4 was substituted in the above procedure for *N*/2 and *N*/8 for *N*/4.

Concentration III. *N*/8 was substituted for *N*/2 and *N*/16 for *N*/4. For convenience, in the case of polysaccharides, n = 1, was taken in the formula $(C_6H_{10}O_5)_n$, under the assumption that these substances are absorbed by the fungus only after they have been hydrolized into hexoses. Figure 3 shows the results.

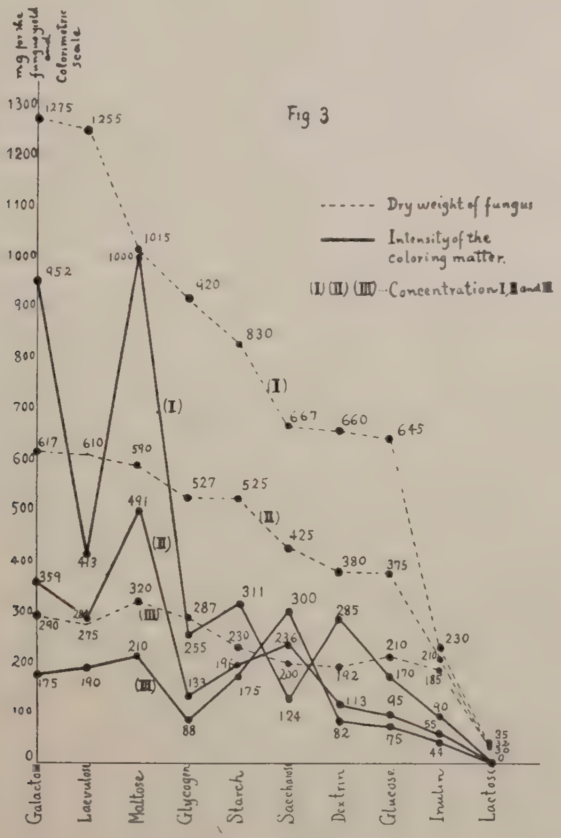
Fig 3

Lactose had absolutely no value and inulin was only slightly effective in both assimilation and the production of colouring matter. Their hydrolization products, galactose and levulose, were very effective. These results were due to the absence of lactase and inulase in this fungus.

Glucose, dextrose, saccharose, starch, glycogen, maltose, levulose, and galactose were good nutrients for the fungus, but they showed different properties in the production of colouring matter. With maltose and galactose the fungus produced its colouring matter very intensively, while with levulose the intensity was lower, although this hexose gave a large yield of fungus. Saccharose was slowly effective and had a peculiar action for the three different concentrations used, the less concentrated gave the greatest intensity of colour, while the influence of al the other carbohydrates upon the assimilation and the production of colouring matter was rather proportional to their concentrations.

Any of these carbohydrates can be material for the formation of colouring matter, if it is possible for the fungus to assimilate them, though their efficiency in such formation is variable.

In general, contrary to the nature of the mineral constituents in the culture media, carbohydrates do not effect the tone of the colour produced but do influence its intensity.

### Influence of oxygen.

In the first stage of the growth, when the spores or the mycelium were sunk into the culture medium, either liquid or solid, the colouring matter was not produced. Later, when some mycelium had reached above the surface of the medium, colouring matter was produced just below the surface. This has been observed previously by WENT (20). At a more advanced stage, the colouring matter was produced either in the submerged or aerial parts of the fungus body, if the medium was favourable for growth. Afterwards the medium became stained by the diffusion of colouring matter, while especially the under side of the floating fungus mass was very intensively stained by the colouring matter within the cells.

In the anaerobic culture, the formation of the colouring matter was greatly hindered, thereby differing considerably from the control, while the growth of fungus occurred to some extent. However, I did not succeed in obtaining a perfectly colourless culture. It is, nevertheless, obvious that oxygen is essential for the production of colouring matter.

### Influence of light.

The production of colouring matter was quite indifferent to the intensity of light. Cultures in the dark and those exposed to the sunlight, both direct and diffused, for the same length of time, showed colour formation and growth of fungus.

### Influence of temperature.

Temperature had a marked influence upon the production of colouring matter as on the growth of the fungus. The optimum temperature was 27° C.—30° C. Above 35° C. and below 20° C., the production of colouring matter was largely checked.

### Influence of water content of medium.

The influence of the water content of solid media was observed and some interesting results were found. For instance, a sterilized and coagulated agar-medium, consisting of 0.5 % $KNO_3$, 0.1 % $KH_2PO_4$, and 0.01 % $MgSO_4$, 3 % maltose, and 2 % agar, which is very favourable for the production of colouring matter, was cut into several square blocks of different sizes and placed in a sterilized Petri dish. Every block was inoculated at the same time. After a few days, the colouring matter was produced more quickly in the small blocks than in the large ones, according to the differences in the rate of evaporation of the water in the blocks.

### Relation between spore formation and the production of colouring matter.

As seen in many cultures under various conditions, the production of colouring matter seemed to follow the formation of spores. It is to be noticed that the colouring matter developed first in the mycelium which produce spores and in the spores, then later in certain mycelium which were rich in reserve material. When colouring matter was intensively produced, the spore formation was also very vigorous. In the culture with lactose medium, in which the fungus remained colourless, spore formation was very slight or lacking altogether.

### Characteristics of the colouring matter.

According to PRINSEN GEERLIGS (14), the chemical nature of the colouring matter of *Monascus purpureus* was considered to be an anthraquinon derivative, and was described as hardly soluble in water and soluble in ethyl alcohol, chloroform, etc., but this investigator used dried material taken from rough cultures on rice medium, in which 0.1 °/₀ arsenic acid was used to avoid the propagation of other organisms. BOORSMA (2), in dealing with its solubility in Na hydrate solution, considered that the colouring matter is made up of two components, $\alpha$- and $\beta$-Oryzaerubin.

Although the present research is not concerned with the chemical nature of the colouring matter, it seems from its physical nature that this colouring matter consists of at least four components, which are produced in both liquid and solid media:

*a*. Water soluble part.
1. Yellow coloured component.
2. Carmine coloured component.

*b*. Water insoluble part, soluble in ethyl alcohol, chloroform, etc.
3. Yellow coloured component.
4. Carmine coloured component.

These four components of the colouring matter seem to be substances closely related chemically, giving fluorescence in their respective solvents.

The proportion of constituents in colouring matter differs according to the environmental conditions; for this reason the tone of the colouring matter varies from yellow to blood red, or carmine, showing various intermediate colours.

It is to be noticed that the colouring matter decreases in solubility when the coloured fungus mass is heated to a temperature above 100° C., or is long dried, so the water soluble part is not obtained. In extracting the Ang-khak mass, some part of the colouring matter which is insoluble in the various solvents always remains. It may be assumed that this was the case in the research of PRINSEN GEERLIGS (14).

For more detailed results, further investigation is necessary.

This research was carried on at the Botanical Laboratory in Utrecht during my visit to Europe.

It is with great appreciation that I thank Professor F. A. F. C. WENT,

who suggested this problem to me and who always helped me with his kind encouragement, as well as putting at my disposal all the facilities of his laboratory.

My thanks are also due to Dr. ANNIE M. HARTSEMA, Mr. S. R. DE BOER, Mr. F. W. WENT, and Miss WILLY M. COELINGH, who often assisted me, and to Mr. P. A. DE BOUTER, who aided me with his mechanical skill.

*Botanical Laboratory.* *Utrecht,* March 1925.

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## **Geology.** — *"On the Direction of the Tertiary Mountain-building Movements in the Island of Java"*, by L. RUTTEN.

(Communicated at the meeting of January 31, 1925).

In the year 1917 the Mining-Department in the Dutch East Indies has undertaken a task of pregnant significance for the knowledge of the geology of the Archipelago. In that year namely the first sheet appeared of the geological map on the scale of 1 : 1000.000 [1]. The accompanying preface [2] informed us, that it was the intention not only to complete this map in 21 sheets, but also to revise the sheets whenever fresh data might be brought forth.

The significance of such maps can be threefold. In the first place, it will often happen that the sketcher detects lacunae in our still very imperfect knowledge of the archipelago, which can be supplied through comparatively little fieldwork. This fieldwork he may then be instructed to execute before finishing the map. Secondly: these maps enable us to note at once the lacunae in our geological knowledge. So for instance BROUWER's map clearly shows the sad state of our knowledge of the islands east of Madura and of the greater part of Sumbawa. Thirdly: such a map may serve as a landmark of our knowledge of the geology of the mapped region; we are thereby enabled to realize at a given moment what conceptions may be derived from the literature. It is true, that this can be attained only if the map is a reliable summary of what is known at a given moment of the region described, and if the designer is well aware that he is a graphical referee of the older literature, and that he should abstain from introducing into the map or into the accompanying profiles his private conceptions, unless they be very carefully thought over. Whereas the first sheet fulfils this condition, it would seem to me that some later sheets do not, and that notably sheet XV (South-Sumatra and West-Java) does not come up to our expectation. The designer, L. J. C. VAN ES [3] has brought forward in the accompanying text two conceptions which are highly disputable, and which at any rate are not fully verified in the literature: in the first place the author's opinion, that the movements which have folded the tertiary deposits of Java have had a North-South trend, and that this trend is still more pronounced in the structures of the older formations, in the second place the author's opinion, that on the basis of our present knowledge of Java and South-Sumatra, a stronger young-miocene folding can generally be distinguished by the side of a less pronounced young pliocene folding.

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[1] H. A. BROUWER, Jaarb. Mijnwezen, 44, 1915. Verh. 2, p. 3—48. With map. *1917.*

[2] E. MIDDELBERG, Ibidem p. 1.

[3] L. J. C. VAN ES, Geol. Overz. kaart van den Nederl. Oost Ind. Archipel, Blad XV. Jaarb. Mijnw. 45, 1916. Verh. 2, p. 55—140, kaart en profielen. *1918.*

In the following pages we shall endeavour to ascertain how far the literature justifies the first opinion of VAN ES.

When propounding the question whether the maps and the descriptions by VERBEEK and FENNEMA [1]) furnish some indication of a definite asymmetry — the expression of a definite direction of the folding movements — of the folds of the preneogene strata, it must be answered in the negative. The map of the Bajah-Coalfield (l. c. Map VIII) does not show enough dip-marks, so that nothing definite can be gathered from them; but from the few definite indications they do give, it would seem that the folds of the eocene strata are symmetrical. The map (l. c. VII) of the vicinity of Tjiletu bay seems to indicate symmetrical folding of the schist-formation; however, the surveys are far too little detailed, so that no definite information can be derived from them. The Djiwo-mountains (l. c. VI) are a far too small and too irregularly defined massif to decide on the trend of the folding movement. The largest massif of pretertiary and eocene in Java, the South-Seraju mountains (l. c. V), distinctly illustrates one thing, viz. that the general strike of the pretertiary and the old-tertiary mountains coincides with the present Java-strike [2]). However, the material available for observation is absolutely insufficient, if we wish to form an opinion about the direction of the folding-movement: in the whole of the pretertiary-eocene territory, measuring 35 × 15 k.m. I see only 15 dip-marks! After VERBEEK and FENNEMA only once a study has been made of the pretertiary strata of Java, viz. by G. NIETHAMMER, who has examined rocks, collected by A. TOBLER in the South-Seraju mountains [3]). NIETHAMMER pictures a profile through the Loh-Uludistrict, which, according information obtained from Dr. A. TOBLER of Basle, is constructed entirely after the data produced by VERBEEK-FENNEMA, and which marks perfectly symmetrical folding of pretertiary and of tertiary. Finally VAN ES himself speaks — also in accordance with the observations by VERBEEK-FENNEMA — of "a broad-arched anticline" in the Tjiletu-region, "with eocene and miocene wings" [4]). I do not see how this consorts with the distinctly isoclinal folding of the pretertiary, indicated in his profils alluded to above.

We, therefore, maintain that the observations in the pretertiary do not at all prove the existence of asymmetrical folding, and that *the intensely isoclinal folding*, which is marked by VAN ES in his profiles (l. c.), and which gives the reader, who is not acquainted with the details, an impression of something real, *is not substantiated by known fact.*

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[1]) R. VERBEEK and R. FENNEMA, Géologie de Java et Madura. 1896.

[2]) This clashes with the earlier conception of the authors (Jaarb. Mw. 1881. I), viz, that the strike of the pretertiary differs from that of the discordant tertiary. This conception, by the way, is no longer adhered to in their map of 1896.

[3]) G. NIETHAMMER. Tscherm. Miner. Petr. Mitt. XXVIII, 1909.

[4]) L. J. C. VAN ES. Jaarb. Mijnw. 46, 1917. Verh. 2, *1919*, p. 29.

The folding in the tertiary requires a more elaborate description. VERBEEK and FENNEMA's work (l. c.) offers but little reliable support, also here. Their profiles are out-of-date; moreover later research has shown that, for obvious reasons, their stratigraphy is at fault on essential points. Still, we wish to point out in the first place that on the profile N$^0$. 30, (region to the North of Solo) a very pronounced northward folding is marked, apparently true to nature. Secondly, that on the profile N$^0$. 58 through the region South of Radjamandala a northward folding has been indicated — for which region, as will appear later on, VAN ES assumes the reverse, viz. a southward folding. However, it should be observed that the observations of the map do not seem, to warrant the detailed profile of fig. 58.

VAN ES's first publication on the geology of a part of *Bantam* [1]) is accompanied by a map and a profile sheet. With regard to the map the author says (p. 191): "On this map have been marked all the data yielded by the exploration, with the exception of those along the Tji-Liman and the Tji Hara.... Further we have taken over the strike-, and dip-marks reported by VERBEEK and FENNEMA". It is clear, therefore, that all the details of the profiles must be justified by the observations on the map. Now profile 2 presents an anticline slightly inclined towards the south, which anticline is a continuation of the Bodjong-manik-ant. However, the section does not stand in absolute harmony with the map. The dip-marks on the map are indicative of a rather considerable complexity: in several localities the Mid. Palembang Layers seem to dip away below the Lower Pal. L,. and in the profile the chief saddle might even be represented declining southward isoclinally, with a southward isoclinal syncline in the Mid. Pal. Layers, joining up in the North. Neither is the extension of the formations in profile 2 in harmony with the map: on the map along the section line the Lower-Pal.-L. and the Mid-Pal.-L. are about of equal breadth; in the profile the Lower-Pal.-L. are about $2^1/_2$ times broader than the Mid-Pal.-L. Also in profile 4 the Bodjong-manik-anticline is represented inclining slightly towards the south, just as in profile 5. But in profile 4 a steep southern wing is altogether absent on the map, which, to be sure, may be expected to contain all the observations. It is true, a steepness in the southern wing is based on a single observation in profile 5, but all the other observations on the southern wing indicate a flat dip, even flatter than on the northern wing. It may very well be possible, therefore, that the southern steep zone is very narrow — that perhaps the one really observed steep dip has only resulted from a fault — in which case the asymmetry of the anticline would be done away with. At all events the number of observations precludes a decision in this respect. The anticline of Bodjong-manik is taken up again in a publication by ZIEGLER, who busies himself with the Bantam coalfields[1]). This author maintains on pp. 55—56 that the southern slope of the principal anticline is steeper than the northern one. Of this asymmetry, however, next to nothing is noticeable in ZIEGLER's profiles. (Pl. IV.) Besides these sections are incorrect in different respects. So for instance the slope of the southern wing of the principal anticline in profile 1 is too steep by 7°, the northern wing, on the other hand is not steep enough. In profile 3 the southern wing again is too steep by an average of 15°, while an entirely unwarranted discordance is marked between Lower-Pal.-L. and Mid.-Pal.-L. On this profile the northern wing is also too steep; likewise the southern wing of the anticline on profile 6. So we see, that the anticline of Bodjong-manik does not present in the profiles the asymmetry for which it is credited in the text. Moreover the southern wing is generally too steep. Finally the fitful changes in the strike of the strata in this district suggest a number of unexplained complications, which render the tectonic more intricate. At any rate there is no proof whatever of a southward inclination of the anticline of Bodjong-manik as might be inferred from the pictures of VAN ES and the text of ZIEGLER.

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[1]) L. J. C. VAN ES. Jaarb. Mijnw. 44, 1915. Verh. 2, *1917.*

In the second part of ZIEGLER's treatise the eocene coalfields on the south coast of Bantam (the Bajah and the Tji Mạndiri field) are discussed. On page 82 we find: "Since the southern wings of the anticlines are generally steeper than the northern, especially in the Tji Mandiri field, we can side with VAN ES in assuming that the push has come from the north". Here again we have to raise some objections: In the profiles of the Bajah-coalfields there is hardly any trace of asymmetry. In profile 2 Pl. V the south wing of the southern anticline is even distinctly less steep than the north wing. Moreover the dips of the south wing are generally overdrawn by 5°. The same applies to the south wing of the most southern anticline in profile 1. On the other hand the slope of the north wing of the most northern anticline in profile 1 is too gentle. If, then, the anticlines in the Bajah-field display a departure from the symmetrical structure, it must be very slight and points rather to an inclination towards the North than towards the South. No more do the profiles of the Tji Mandiri field (Pl. VI) reveal any pronounced push from the North; moreover the maps are only provisional and the condition is very complicated. Only the northern anticline of profile 2 furnishes indications of asymmetry, but here again the northern wing should be drawn steeper. But ZIEGLER's profiles through the Tji Mandiri field induce us to revert to VAN ES's publication of 1918 (Jaarb. 1916), the direct motive for our criticism. As stated above, VAN ES's "Survey-map" is accompanied by a sheet with profiles, which illustrate a southward folding movement. As regards the folding in the tertiary, the most suggestive part is the southern part of profile 5, on which in the eomiocene two saddles are represented inclining very much towards the South. The text says: "The eocene.... forms two.... anticlines, of which the southern wing is much more inclined than the northern". (page 66).

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[1]) K. ZIEGLER. Jaarb. Mijnw. 47, 1918. Verh. 1. *1920.*

Now, as appears from the place-names, the profile of VAN ES must be situated just between ZIEGLER's profiles I and II through the Tji Mandiri field. We, therefore, considered it well worth, to compare them: in the subjoined diagram the profile of VAN ES is represented between those of ZIEGLER. They are on the same scale. For better comparison I have drawn ZIEGLER's profiles to a greater depth, while sticking faithfully to his interpretation of the facts. It will strike the reader at once that VAN ES's profile does not at all resemble those of ZIEGLER — which have been constructed from a large number of observations. His southern asymmetrical anticline, the south wing of which is, indeed, marked below the sea-level, is to give place to a set of at least 4 steep, symmetrical closely folded saddles [1]; the more northern, highly asymmetrical syncline of VAN ES is on both profiles of ZIEGLER a fairly symmetrical syncline. Only the most northern anticline of VAN ES is represented asymmetrical with a steep south wing on ZIEGLER's profile II. However, on profile I it is already represented differently, although here an upthrow of miocene, leaning against eocene is represented which, however, is merely a theoretical interpretation. As for profile II we have to point to two facts. In the first place on ZIEGLER's profile at the very least two anticlines are missing (they may indeed be read from his map, but they are absent on the profile). In the second place the anomalous contact between eocene and miocene, as drawn by ZIEGLER, is entirely theoretical, so that the whole saddle might as well have been made symmetrical by drawing the eocene strata on the north wing steeper in the depth and by adding eventually a northward upthrow of the south wing overlapping the north wing. In the third place at *D* ZIEGLER's profile is not at all in keeping with the facts, which point to considerable complication. It may still be pointed out, that the profiles I and II, which are by no means alike, are separated only by three k.m., which is suggestive of strong complication in the lower strata. Only by dint of very detailed work would it be possible to elucidate the tectonic and could an answer be given to the question whether the structures follow a definite trend here.

At all events we feel justified in stating *that the asymmetrical structures as suggested by profile 5 of* VAN ES *are not supported by any real fact, neither as regards the representation of the tertiary, nor as regards that of the pretertiary.*

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[1] In this profile II near *A* ZIEGLER has drawn one anticline less than has been marked on his map.

ZIEGLER has produced remarkable sections of the Tji-Ditik Leutik, north of the Bajah-field. First of all he gives us of this district (p. 125) a distinct southward upthrust of a coal-layer, but the text (p. 124) gives us the impression that even here the upthrust is not an ascertained fact. [1])

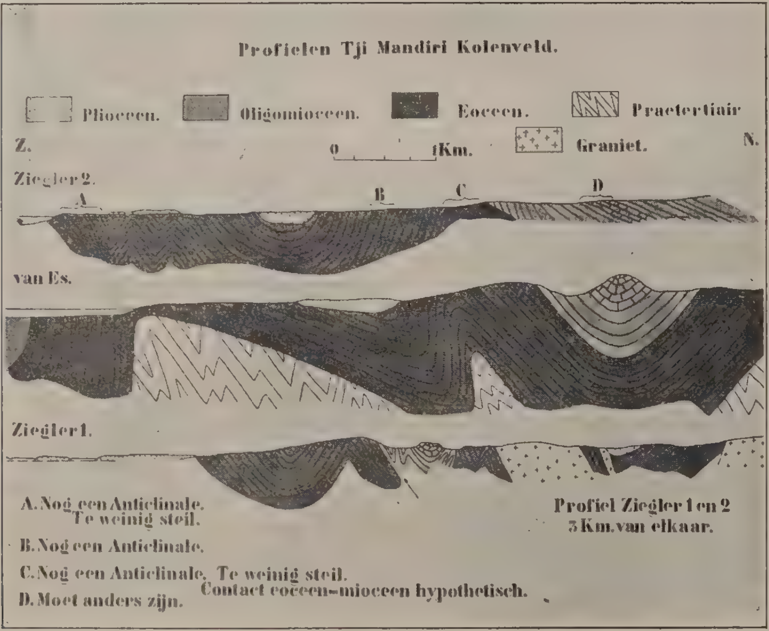
Profielen Tji Mandiri Kolenveld.
Plioceen.
Oligomioceen.
Eoceen.
Praetertiair
Graniet.
Z.
N.
0
1Km.
Ziegler 2.
A
B
C
D
van Es.
Ziegler 1.
A. Nog een Anticlinale. Te weinig steil.
B. Nog een Anticlinale.
C. Nog een Anticlinale. Te weinig steil.
D. Moet anders zijn.
Contact eoceen–mioceen hypothetisch.
Profiel Ziegler 1 en 2 3 Km. van elkaar.

Fig. 1.

The whole upthrust, however, is of no general interest, it regards details only; similar small disturbances will ever occur, howsoever the folding movement may have trended. Of far more essential significance is a profile of some kilometers in length reproduced on p. 125, on which are represented a southwardly inclined syncline with a nucleus of miocene followed in the North by an equally southwardly inclined anticline with an eocene nucleus. This profile *may* be in accordance with the observations on the map, but the text again says: "In fig. 2 . . . . . . we have endeavoured to schematize the situation". It appears then that there is some uncertainty also here.

Three things we have to bring into prominence:

1°. that this overfolding, occurring over a small tract, would be an isolated case in a region of symmetrical folds;

2°. that this overfolding would occur on the northern wing of a huge anticline, of which the profile is represented perfectly normal only 1 k.m. to the west of the critical point (see fig. 2);

3°. that the sketched profile with the twofold overfolding is not only incompatible with the condition at 1 k.m. to the West, but that also to the East the situation soon changes completely. We see, therefore, that an intense southward push in this region is *not a positive fact*, which ZIEGLER himself admits. With almost equal reason we might apply the local relations, reported by VAN ES on the northern margin of the anticline of Bodjong-manik (ante p. 193 line 19—15 from the bottom), to prove that in that locality a sharp northward overfolding occurs. Still, this very instance has been mentioned by VAN ES as the most cogent evidence of a southward fold: "Most likely the eocene has been pushed over the more southern oligocene-old miocene orbitoidal limestones of the northern wing of the following anticline" (l.c. 1918 p. 66), and: "However, there are two instances in West-Java which prove distinctly that the first statement (folding-pressure from the North) is correct. These instances are the structure of the most southern anticline near Sukabumi and the anticline of Tji-Djengkol in Bantam (Tji-Ditik Leutic district). It has been *demonstrated* for the first instance by myself, and for the second by ZIEGLER, in the field, that the southern wing has been crushed and that here even an overthrust has occurred in which the pushing force can have come from the North only"[1]) (l.c. 1919 p. 48).

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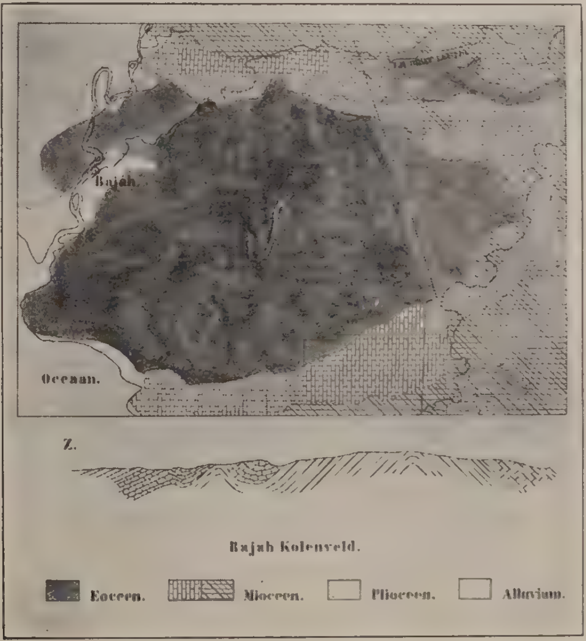
[1]) "So that presumably we have to do here with a fault".



After K. ZIEGLER. 1920.

Fig. 2.

In the treatises by VAN ES of 1918 and 1919 one more instance is mentioned of a saddle in West-Java, which is considered as yielding clear evidence of a southward folding movement. It is the above mentioned anticline to the South of Sukabumi, through which VAN ES has also reproduced a profile (l. c. 1918, northern part profile 3), which is indeed very suggestive (See Fig. 3). The profile runs right over G. Walang, to the South-West of Sukabumi, which is just the „Critical point" in the profile. On closer inspection, however, various objections may be raised also here. In the first place the deeper portion of the profile, which is highly suggestive, and in which again the isoclinally folded pretertiary has been pictured, is purely theoretical. In the second place the surveys on the south wing, which should justify so sharply inclined a profile as VAN ES has pictured, have not been carried out, because, according to his own sketch, and also according to the map of VERBEEK-FENNEMA (l. c.) and that by HOOZE[1]) the tertiary is here overlain by volcanic formations and by diluvium. Furthermore, VAN ES's representation does not consort with the data produced by VERBEEK-FENNEMA (l.c.) who mark on the G. WALANG a perpendicular position of the layers. Neither does it consort with those of HOOZE (l. c.), from whose numerous observations — even when making allowance for his still primitive notions of stratigraphy — a section might be constructed far different from that of VAN ES. Now it may very well be the case, that VAN ES has observed facts which account for the northern part of his profile, but when he applies them to set at rest such a problem of principle as the southward folding-movement in the tertiary of Java, he might certainly have stated how far and why the observations of earlier explorers which no doubt are not without relative value, are to be interpreted in a different way. When considering that the excessively overlaid South wing is not verified by observations and that, in accordance with older data, the North wing may look different from VAN ES's section, it is difficult to reasonably conceive an overlaid- to overthrusted

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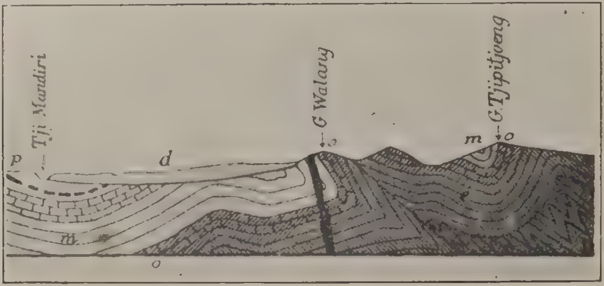
[1]) The marking in brackets and the italics is mine.



After L. VAN ES. 1918.
Fig. 3.

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[1]) J. HOOZE, Jaarb. Mijnw. 1882. (Scientific section).

saddle. At best we may be safe in maintaining that the anticline of G. Walang possibly possesses a steep zône on the South margin. But let it be remembered in this connection that VERBEEK—FENNEMA (ante p. 193) have sketched some tens of kilometres to the east a profile through the same anticlinal region with a northwardly trended overfolding.

Now when looking once more at the four survey-profiles, recorded by VAN ES in 1918, we are bound to say that N<sup>0</sup>. 4 (Tji-Mandirifield) has lost its suggestive significance, while at the same time the northern portion of profile 3 (G. Walang) cannot afford cogent evidence for a southwardly trended folding. For a single anticline — and that a doubtful one — with a southern steep zone, or even with a southward overfolding does not yet establish a folding movement directed southward [1]). Profile 1 does not suggest anything, so that only profile 2 and the southern part of the profile 3 are left for discussion. As regards the southern part of profile 3, there is only one locality that implies a slightly southward push, viz. the anticline of Bodjong-Lopang with its steep south limb. I feel inclined to say that also here the condition cannot be quite correct. First of all a steep northward slope occurs on the map of VERBEEK—FENNEMA [2]) also north of Bodjong Lopang, and secondly: in 1912 I visited the vicinity of Bodjong Lopang and found a northward slope of limestones and marlstones in various localities south of the village in the district where according to VAN ES exclusively southward slopes occur. Lastly, as to the profile 2, two remarks have to be made. To the North of Tjipanenga, where a saddle is marked inclining slightly southward, the situation is altogether out of keeping with the map of VERBEEK—FENNEMA and with their profile N<sup>0</sup>. 55, resulting from a number of observations on the map. Between Tjipanenga and Sign. Tjilentab (about the end of VAN ES's profile) VERBEEK and FENNEMA mark three steep, symmetrical anticlines. Here VAN ES's profile presents the peculiar fact of a limestone layer of 300 m. rhickness, thinning out completely over a distance of 1 km., which must be considered highly improbable.

Also to the South of Tjipanenga and the North of Pasir Soeren the situation must be more complicated than is indicated by VAN ES, as the surveys of VERBEEK—FENNEMA go to show. In the second place according to VAN ES strata occur to the North of the Tji Odeng in the miocene whose thickness grows up to 300 m. over a distance of not quite 2 km. This again implies that the profile is far from being absolutely accurate. This does not preclude the possibility that the anticline of the Tji Mandiri will have a steep south limb.

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[1]) We are reminded here of many instances in Palembang and Djambi of anticlines with alternating southwesterly and northeasterly steep zone, which alternation may even be traced on one and the same anticline. Or we may compare recent profiles from the Swiss Jura e.g. BUXTORFF Geol. Grenchenbergtunnel, 1917, or ELBER, Verh. Natf. Ges. Basel. 32, 1920.

[2]) To be sure I know that VERBEEK and FENNEMA's map is often deficient, but on the other hand the positive data expressed in the map in the form of dip-marks, are almost always correct.

In his publication of 1919 VAN ES (p. 48) says: "From the shape of the anticlines, of which the south wing is generally steeper than the north wing, we are to conclude that the folding pressure has come from the North". It is impossible, after an examination of the available body of facts, to apply this statement to West-Java for which we rather have to conclude: "*The anticlines in West-Java hitherto known are sometimes broad-arched, sometimes closely folded, but mostly symmetrical. It is probable that there are a few with a steep south wing, but this has not been satisfactorily established for any of them through detailed research. For a determination of a definite direction of the folding movement adequate data are lacking.*"

After having ascertained whether any information may be got about the presence of asymmetrical foldings in the tertiary, from the recent explorations of VAN ES and ZIEGLER, we still have to inquire how far earlier publications on Java can furnish any elucidation on that head. A few years back C. 'T HOEN published¹) fairly detailed maps and profiles about a tract in North-Rembang. The anticline of Ngandang-Lodan sketched on these maps presents a feeble, though unmistakable overfolding towards the North, and the same may be said of the less known anticline to the West of the G. Butak. It must be added directly that explorations by oil-geologists have brought to light other anticlines in North-Rembang, much more sharply overfolded in a northern direction, but that, on the other hand, there have been detected saddles, that have been intensely overfolded towards the South. Furthermore an anticline has been discovered in the vicinity of Soerabaya, which displays in various localities a northward, in others a southward overfolding.²) In a previous paper I have pictured four profiles from the western part of the residence of Soerabaya and more westerly regions³) on which the anticlines of Kabuh and Kambangan reveal unquestionable northward overfolding. In addition it may be observed that at the very least on six profiles the presence was established of a steep north limb and a much more horizontal south limb at the anticline of Kambangan. The profile N⁰. 4, via Ngawi, where the folding culminates, and where a folding towards the South would be expected if there were any tendency for it, reveals no indication of such a tendency; there is rather an inclination for northward overfolding. This is the more striking as this profile has been derived from as many as 60 observations, made along the cross-section. Finally broad-arched folding with symmetrical saddle-structure has been recorded from the tertiary region to the North-East of Buitenzorg.⁴)

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¹) C. 'T HOEN. Jaarb. Mijnw. 45, 1916. Verh. 2, *1918*.

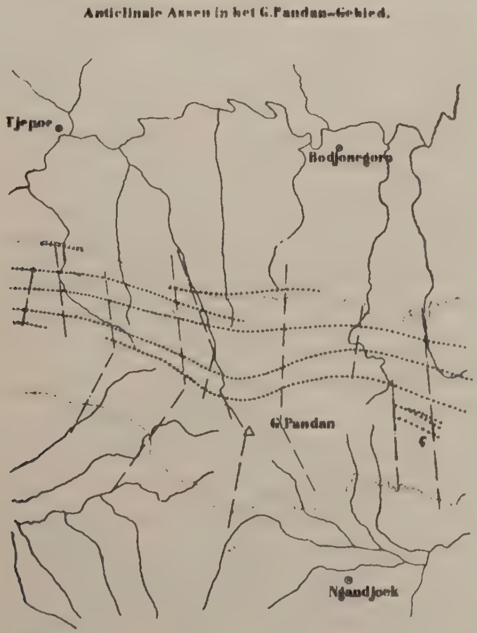
²) W. HOTZ u. L. RUTTEN, Zeitschr. f. prakt. Geol. 1915.

³) L. RUTTEN, Verh. Geol. Mijnb. Gen. Geol. Serie III, 1916.

⁴) L. RUTTEN, These Proceedings 1917.

In the preceding lines we have passed in review the most important literature concerning Java. *We see from it that it contains no indications of a definite direction of the tertiary folding movements.* There are indications of a northward movement in East-Java, and a southward movement in West-Java, but they are too feeble to warrant a decision.

However, a few unpublished surveys may still remove the uncertainty. We alluded to it just now that the miocene marl zône, which reaches from Soerabaya as far as the western boundary of Semarang, or perhaps farther, is often characterised by an intense compression, so that if the folding of the Javan tertiary should have had a definite direction, some indication of it might be expected here. It has also been alluded to, that the profile via Ngawi shows a northern trend, small though it may be. Now it appears that the intensity of the folding in the marl-zône increases from East to West. In the year 1912 Dr. W. HOTZ of Basle and myself surveyed a large number of profiles with a view to study the structures. The surveys between the western boundary of Semarang and the meridian of Purwodadi were performed by HOTZ, those to the East of the Solo-river chiefly by myself; three profiles in the neighbourhood of the Pandan-massif were mapped by us in cooperation. Some of these profiles have already been published previously (HOTZ-RUTTEN l.c., RUTTEN l.c., 1916). It may generally be stated here that on HOTZ's profiles as well as on mine overfolding towards the North is of much more frequent occurrence than towards the South. Now, there



After surveys by W. HOTZ and L. RUTTEN.
++++ Anticlinal axis.
Fig. 4.

is a method to ascertain which conclusion the profiles may impart regarding the direction of the folding movements without reproducing the sections, which, indeed, naturally always entail a certain amount of subjective interpretation. With symmetrical folding in E.W. trended mountains the chances of a northward and a southward dip are of course equal. When the overfolding proceeds in a northern direction the chance of finding a southward dip will gradually become greater, until with perfectly isoclinal folding the chance of a southward dip has increased up to 100 $^0/_0$. In case of overfolding towards the South the reverse will take place. The phenomenon will be the more conspicuous as the number of anticlines on a profile increases. On the profiles under consideration this number is rather large. I have counted the observations made by HOTZ and myself separately (together on 30 profiles) to the following effect, the starting number being 100 southward dips:

| | Southward dip | Northw. dip |
|---|---|---|
| HOTZ | 100 | 60 |
| RUTTEN | 100 | 63 |

These numbers, relating to more than 800 observations, speak volumes In the first place they are a striking illustration of the fact that the surveys, which were performed by us separately yield an almost equal percentage of northward dips. *In the second place that the southward dips far outnumber the northern (to the ratio of* 100 : 62*) which implies a northward folding movement.*

This numerical evidence I conceive to be of vital importance. In addition I wish to add another argument for the northward folding movement in East-Java. The three profiles in the Pandan territory, jointly explored by HOTZ and myself, yielded a curious effect, viz. that to the East of G. Pandan the anticlines tend to bend away towards the South-West whilst to the West of G. Pandan, they curve northward, then again resume their normal direction (approximately E.-W., with a slight departure towards the North). It must be noted that the anticlines referred to run north of the Pandan massif. It is evidenced by the survey, that, at the time of the folding, the large volcanic mass of the G. Pandan must be admitted to have existed already.

Well then, the situation described is readily explained when conceiving the folding movement to have been directed towards the North, through which the plastic marls to the East and to the West of G. Pandan could shift farther towards the North than the rigid Pandan massif itself and the marls lying in its „shadow". If the direction of the folding had been southward a far different course of the anticlinal axes around the G. Pandan would be expected. *Also the course of the anticlinal axes in the neighbourhood of the Pandan massif favours the hypothesis of the existence of northward folding movements in East-Java.*

It is not expedient to apply this pronouncement to West-Java, where southward movement is not precluded. However, there is something else. According to TOBLER the direction of the folding movement in Sumatra has been from S.-W. to N.-E., from the Indian Ocean to the old Sunda-continent. This hypothesis is based on the fact that in large tracts of Djambi and in adjacent regions the pretertiary strata have been folded distinctly isoclinally with S.-W. dips [1]). This hypothesis can hardly be contended, although this does not mean to say that we have *to adopt unreservedly* TOBLER's views [2]) as regards a structure of overthrust-sheets in Djambi. If it should appear now that the folding in Central and East-Java points to the same direction of movement — towards Sundaland — as that in Central Sumatra, it is very probable that the same direction will have existed along the western and the southern margin of Sundaland, and that it will also exist in West-Java.

In conclusion I wish to call attention to the fact that on SCHÜRMANN's map of Borneo the folding movement of Macassar Strait is represented directed towards Sundaland, although for Java SCHÜRMANN adopts VAN ES's view that the direction was southward there [3]).

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[1]) A.o. A. TOBLER, Djambi verslag, 1924, p. 439.

[2]) The arguments adduced by VAN ES (l. c. 1919, p. 107) for westward overthrusts in Sumatra, are in my opinion very weak; for one thing the divergence of the Sumatra-coulisses may remind one of normal virgation, and suppose we can imagine an overthrust here, we may just as well construct the trend of it towards the East as towards the West.

[3]) H. SCHÜRMANN, Geol. Rundschau, XIV, 3, 1924.

**Anatomy.** — *"On the existence of a dolichocephalic race of Gorilla".*
By Prof. L. BOLK.

(Communicated at the meeting of March 28, 1925).

The discovery of a fossilized not fully grown part of an anthropoid skull at Taungs (South Africa), has rightly awakened general interest; moreover whereas the discoverer — Prof. DART of the university of Witwatersrand (Johannesburg) ascribes the found fossil as belonging to an extinct primate group: "Intermediate between living anthropoids and man [1]).

It would be rather premature, already to judge the biological importance of the found object, on the ground of the very short description given by DART. For this we will have to wait until the promised detailed description is at hand, after the discoverer will have had the opportunity of comparing the infantile skull of the Australopithecus africanus, so named by him, with equally old infantile skulls of the still living Anthropomorphs. It is not unlikely that by this comparison the obvious enthusiasm, wherewith the discoverer views his discovery, and of which his conclusions at present clearly manifest, will have to give place to a more composed criticism and objective judgment. It will in no way wrong the great importance of the discovery; more likely it will do justice to its true morphological significance.

The description of the object by DART, and principally the main arguments, which he gives for his opinion viz. that the new form "exhibits an extinct race of apes intermediate between living anthropoids and man" prompts me to give a short description of a skull, through which our knowledge of the present living Gorilla races is extended and through which the judgment of the morphological importance of the Australopithecus skull may be more accurate.

The discoverer begins his description by pointing out "that the whole cranium displays *humanoid* rather than anthropoid lineaments. It is markedly dolichocephalic and leptoprosopic". The first — and as regards the skeleton — the most prominent human attribute of the new form, the longheadedness, together with a long and narrow face is stated.

To what extent this attribute of the Australopithecus forms an antithesis to the present living man-ape, is known to every morphologist, who more especially studies the comparative anatomy of the Anthropoids.

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[1]) RAYMOND A. DART. Australopithecus africanus: The man-ape of South-Africa. Nature, February 7, 1925.

In the critic of the fossilized remains of the Australopithecus by KEITH (Nature Febr. 14, 1925), he especially lays stress on this attribute. He writes: "Even if it be admitted that the Australopithecus is an anthropoid ape, it is a very remarkable one. It is a true longheaded or dolichocephalic anthropoid — the first so far known".

Seeing that the type of the skull of the Australopithecus promises to play an important part in the discussion on the place of this form in the system, I considered it desirable, to draw the attention to the fact, that also among the present living Gorillas, a race is found, which is strongly dolichocephalic and leptoprosopic and shows both these qualities to the same high degree as the fossil of the Australopithecus. This race is evidently only few in number.

Amongst the 50 Gorilla skulls in the Anatomical Museum of the University of Amsterdam only one example of this race is present. This skull is conspicuous on account of its outstanding difference from the rest. To what degree this is so, will be seen from what follows.

The skulls present in the above named museum are partly derived from Camerun and partly from the French Congo. The last named group was obtained throughout years by the intercession of the firm TRAMOND in Paris.

Some years ago this firm again informed me that they held at their disposal three skulls for the museum, "dont un d'une forme particulière". I mention this detail in order to show, how strongly the shape of this skull differs from the rest. That its characteristic shape is due to its strongly dolichocephalic and leptoprosopic nature, I immediately noticed on receiving it.

I never till now could execute my intention of giving a description of this object, but the discovery of the dolichocephalic Australopithecus prompts me not to wait any longer.

In order to assure an easy comparison, next to the sketch of the dolichocephalic skull a conformable sketch of the skull of a common brachycephalic Gorilla, will be placed.

In fig. 1 the norma verticalis of the dolichocephalic form is sketched, in fig. 2 that of the brachycephalic. The terms dolichocephalic and brachycephalic, are not truly applicable, in that the index cephalicus is not taken in the same way from full grown Gorillas as from man. As regards the greatest breadth of the cranium, this could if need be, be determined in a comparative way with that in man, but the greatest length is not to be determined, because the strongly developed crista occipitalis in the occipital region and the more strongly developed crista supraorbitalis in the frontal region, make an accurate measurement of the true length of the skull impossible.

Only in infantile skulls, where the crista occipitalis is wanting, the orbits still situated subcerebral [1]) and the frontal eminence still absent, it is possible to determine an index cephalicus.

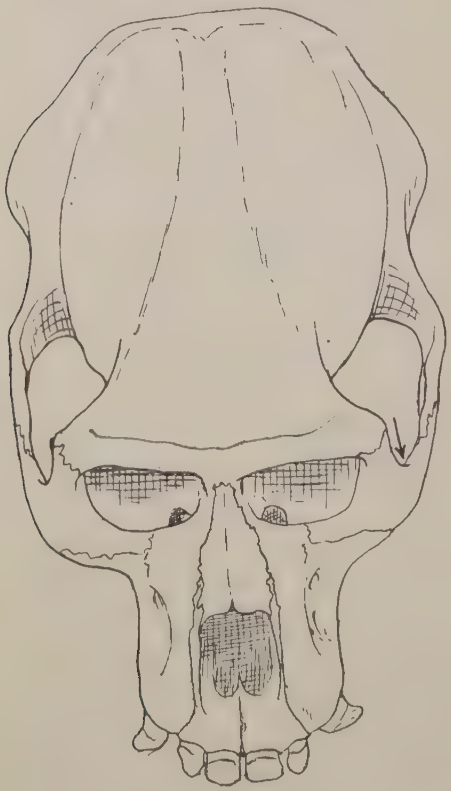

Fig. 1.

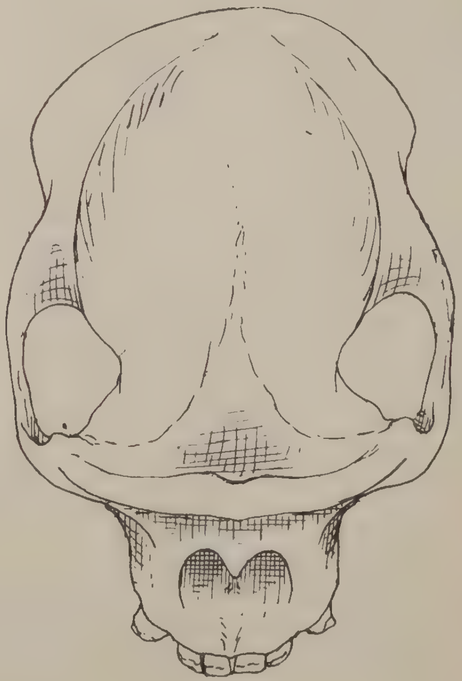

Fig. 2.

In the adult skull the index encephalicus i. e. the length-breadth-relation of the cranial cavity, which is easily to be determined in a sagittal section of the skull, should be used instead of the index cephalicus.

Although the difference in type between the skulls in figs. 1 and 2 is not to be expressed by the value of the index cephalicus, a comparison between both figures leaves no doubt about the essential difference in shape. Both skulls have been drawn, with the arcus zygomaticus running horizontally.

It is immediately evident, that together with the long, narrow cranium of the one specimen, we also find a long and narrow face, while the other object not only has a short round skull, but is also characterized by a short broad face. To this harmonical relation between the shape of cranium and face, the concurrency of dolichocephaly and leptoprosopy, which was also established in the Australopithecus by DART, this author especially draws attention to.

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[1]) As regards the origin of the supraorbital cristae, the result of the forward shifting of the orbits, see my communication about the significance of the frontal ridges in the Primates. These Proceedings 25, 1922.

We will now study the facial part of the skull more closely. The leptoprosopy in the dolichocephalic Gorilla is the result of two causes, which is easily pointed out by the comparison of figs. 3 and 4. It

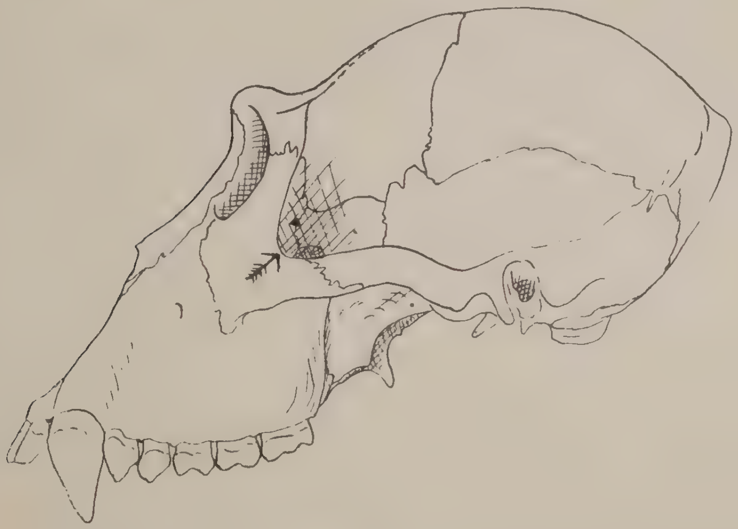

Fig. 3.

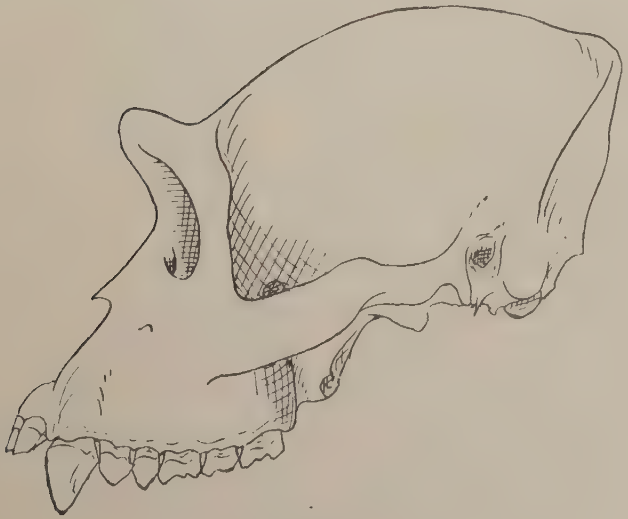

Fig. 4.

follows from measurements, that a true lengthening of the face has taken place. But this cause — about which presently more — is not the only. The leptoprosopy was partly brought about because the base of the face — the palate therefore — was as a whole, pushed horizontally in a frontal direction. This appears to be so, on account of different anatomical peculiarities, but is most clearly demonstrated by drawing a line perpendicularly down from the highest point of the crista supra-orbitalis. In the brachycephalic skull, this line passes through the row of teeth viz. through 1st molar. In the dolichocephalic skull, however, the whole row of teeth lies in front of this line.

As a result of this displacement of the bottom of the face, the facial part of the skull is stretched in length, and has thus acquired a profile, which strongly differs from that of the ordinary Gorilla skull.

The same cause is also to same extent responsible for the difference in the direction of the plane of entrance of the orbits. In the common skull, as appears from figs. 2 and 4 this direction is rather vertically. In the dolichocephalic skull, however, the lower margin of the orbits strongly inclines to the front. The forwardly inclined pterygo-maxillary suture in this skull, in opposition to the vertically directed in the chamaeprosopic type, also is the result of the shifting of the facial base forwardly. In conclusion attention is still drawn to the strongly developed lamina externa, of the Pterygoid, through which the fossa pterygoidea is shaped into a form strongly resembling that of the human skull. I lay stress upon these points because, as said, the skull of Australopithecus also is leptoprosopic. The drawings, however, of this object lead us to suppose that in this case the leptoprosopy is caused in the main by the narrowness of the facial skeleton, for there is nothing to see about a shifting of the palate as is the case in our Gorilla. Therefore the profile of the Australopithecus differs strongly from that of the leptoprosopic Gorilla. From a comparison between both, no conclusion may however be drawn, the profile of the fossil having still an infantile character.

That, however, the leptoprosopy in our Gorilla is not only due to the lengthening of the face, but has to a large extent the same cause on which the leptoprosopy of the Australopithecus depends, viz. the narrowness of the facial skull, will now be shown.

An impression of the difference between the physionomic aspect of the common Gorilla skull and that of the dolichocephalic form, is acquired by a comparison of figs. 5 and 6. To get a more precise insight into these differences, it is desirable to take a few measurements, and to compare the resulting facial index of the ordinary skull with that of the long headed variety. When one intents to use measurements and indices in order to point out individual differences in the Gorilla, it is not possible to apply the usual measurements of the craniometric system of the human skull. This system has originated in accordance with the shape and structural properties of this skull. The strongly different Gorilla skull, however, requires an own craniometric system. This has already appeared to be so in the index cephalicus, which in the Gorilla cannot be determined in the same way as in man. In the Gorilla, an exact consideration is also necessary to find the appropriate measurements and method through which the individual differences may be stated accurately by numbers and numerical relations.

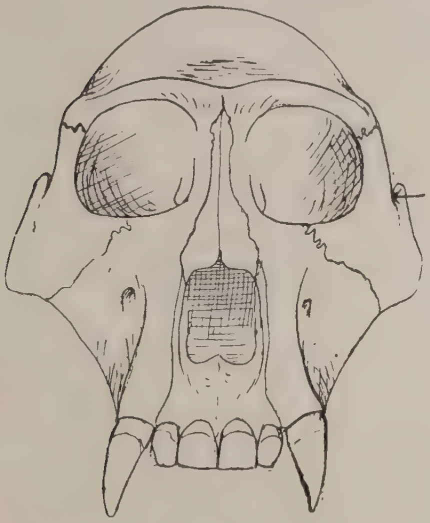

Fig. 5.

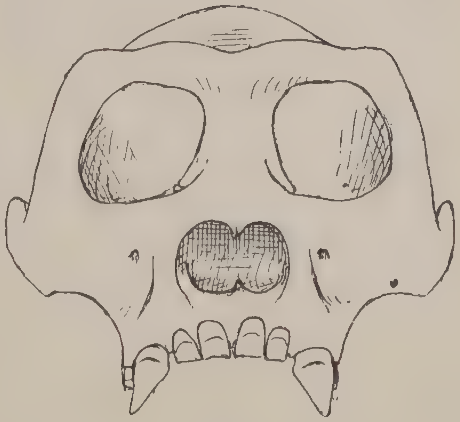

Fig. 6.

As regards the facial skeleton, both the following measurements appear to me the most recommendable to express the facial index. The greatest breadth is taken between the points where the upper margin of the zygomatic arch bends itself round into the lateral orbital margin. This point is represented by a little arrow in figs. 1, 3 and 5. As the greatest length we may take that of the profile, i.e. the distance measured in the median line between the highest point of the Crista orbitalis and the front margin of the intermaxillare between the median incisors.

I have determined the length and breadth of the face of 43 adult Gorilla skulls in this way and calculated the index facialis according to the formula $\frac{100B}{L.} =$ index facialis.

That in the dolichocephalic Gorilla, we indeed have to deal with a separate race, appears convincingly from the fact that with no exception the width of the face of the common Gorilla is greater than its length. The index facialis is therefore always greater than 100. In the dolichocephalic skull, however, the relation is vice versa, the breadth — 120 m.M. is considerably less than the length — 134 m.M. The index facialis is therefore less than 100.

In this short communication it is superfluous to state, in extenso, the measures and the resulting indices of the measured skulls. It is sufficient if I give the general result of my measurements. While the index facialis of the dolichocephalic Gorilla is 89.5, it varied between 103.4 and 122.6 with an average of 111.5 in the common type.

The index facialis of the dolichocephalic skull is therefore much below the variability of the common type. The dolichocephalic skull is therefore not an extreme individual variation of this type, but a true variant of the species with a specific attribute, f.i. a marked leptoprosopy.

As regards the absolute measures it is to be noticed that in the chamaeprosopic type individuals occurred, whose facial breadth was less than that of the leptoprosopic specimen, but they were small female individuals. On the other hand again, some very large skulls, of which the absolute length surpassed that of the leptoprosopic form, are present in the collection. This will become evident from what follows. The face of the leptoprosopic skull was 120 m.M. accross and 134 m.M. long. The common skulls varied from 116—170 m.M. accross, with an average of 146 m.M., and the length between 101 and 154 m.M. with an average of 131 m.M.

From these figures it now clearly appears, that the leptoprosopy of the dolichocephalic skull is not only due to an increase in the length of the face as a result of the shifting already treated, but also in account of a decrease in the breadth. Because whereas the length is only a little more than the average length of the common skulls i. e. 134: 131 m.M., the breadth is considerably less i. e. — 120: 146 m.M.

The narrowness of the face is no primary structural property of the skull, it is an adaptation to the dolichocephalic nature of its braincase because a smaller crane necessarily has a smaller base, also in its forepart, to which the facial part is affixed. Dolichocephaly therefore is the primary and leptoprosopy is the secundary consequence of it, through which the harmonical shape of the whole skull is brought about. The narrowness of the face is associated with the somewhat deviating shape of the orbits from the ordinary. Just as in the Australopithecus they are less angled. And as a further harmonic association the entrance to the nasal cavity is long and narrow. These and still other details are clearly seen by a comparison of figs. 5 and 6.

It was evident, that in accordance with the narrowness of the maxillo-orbital part of the face and the base of the skull, the mandible would also be narrower. The comparative investigation has shown this to be so. In this comparison the greatest breadth of the mandible was taken as the distance between both the lateral margins of the condyles. This measure is shown as a dotted line in fig. 7. This dimension, at the same time, gives an impression of the breadth of the base of the skull, as it is identical to the greatest breadth between the two Fossae glenoidales. The greatest length of the mandible was determined as the distance from the Incision to a line drawn perpendicularly from the middle of the line, joining the posterior margins of the capitula mandibulae. This measure is also represented by a dotted line in fig. 7. The index mandibularis was calculated from the obtained measures to the following way: length ÷ 100 × breadth. For 41 common skulls this index varied between

82.7 and 103.3, while it was 71.6 in the mandible of the dolichocephalic skull. There is therefore again a great difference between the relative smallest mandible of the common skulls and those of the particular form, which is a quite apart specimen.

It has already been stated, that it is not possible to determine an index cephalicus from the adult Gorilla skulls, because during growth the orbits shift themselves in frontal direction, and thus make it impossible to determine the true length of the cranium. The form of the cranium, thus has to be expressed by an index other than the index cephalicus. The most suitable for this is the index encephalicus i.e. the relation between the greatest length and breadth of the cranial cavity. These measurements may be determined quite accurately from skulls sagitally bisected.

As points from which the greatest length of the cranial cavity must be determined, I have in previous communications recommended and applied the Fronton and Occipiton. In literature it is usually wrongly stated that in anthropoids during growth, the frontal part of the braincase is flattened off, through which the frontal vault disappears. This conception is wrong. The vaulting of the frontal region which is externally so clearly seen in the infantile skull of the anthropoids, in reality persists throughout life, but externally this vault is covered, because during the growth the orbits, which originally are situated beneath the brain, even as in man, i.e. beneath the base of the skull are displaced to the front, so that they come to lie anterior to the frontal vault. As a result of this displacement, the orbita receives a new roof, which grows out from the frontal wall of the skull [1]). One can show this quite easily on a sagitally bisected skull of a full grown Gorilla, the internal surface of the frontal region is not vaulted less in

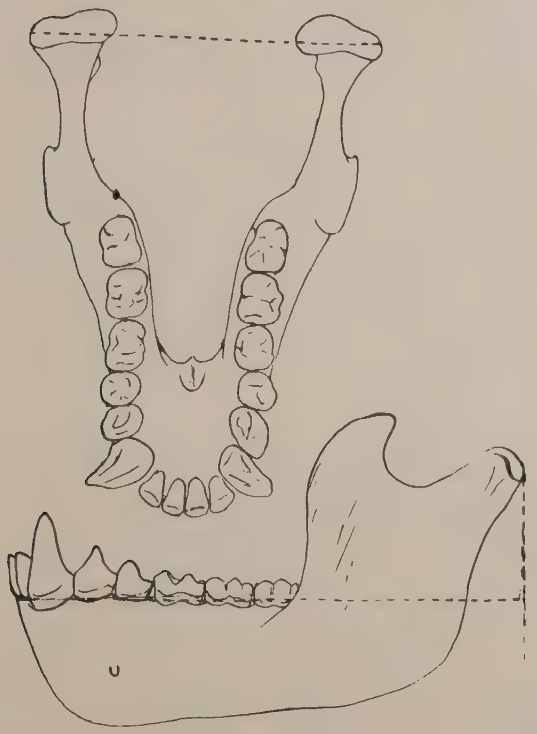

Fig. 7.

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[1]) See my communication: Die Topographie der Orbita beim Menschen und Anthropoïden und ihre Bedeutung für die Frage nach der Beziehung zwischen Menschen- und Affenschädel. Verhand. Kon. Akad. v. Wetensch. 2e Sectie, Deel XX. 1919.

such a skull than in an infantile one. Vide f.i. the mediagramms of both the skulls in figs. 8 and 9.

In the mentioned communication the point where the frontal wall and the base of the skull meet in the median line, was termed as Fronton.

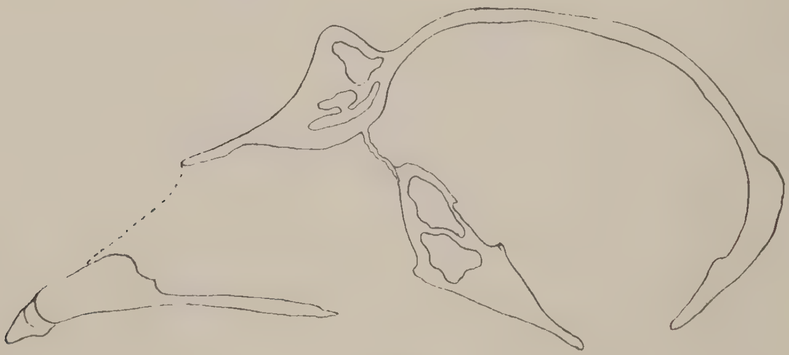

Fig. 8.

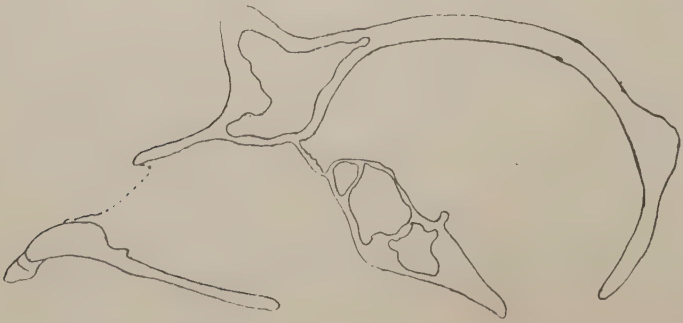

Fig. 9.

As Occipiton was termed the point on the occipital surface of the inner wall most distant from the Fronton. Between both these points is found the greatest length of the cranial cavity. For the greatest breadth add the greatest depth of the cranial cavity of each of the two halves together.

In this way I have determined length and breadth of the cranial cavities in 10 skulls, and calculated the index encephalicus. This varied between 80.6 and 85.9. This therefore confirms the known fact, that the Gorilla is brachycephalic. The index encephalicus of our particular skull again strongly differs from this. The length of the cavum cranii was 127 m.M., the breadth 92 m.M., the index therefore was 72.4.

This index only differs to a small extent from that which KEITH determined for the Australopithecus africanus, i.e. 71.

As regards the capacity of the dolichocephalic skull the following may be mentioned. The capacity of the anthropoid skulls, which are in the Anatomical Museum of the University of Amsterdam, has been determined by one of my assistents[1]) and as regards the Gorilla skulls, he got the following results.

*Capacity of the Gorilla-skull*:

| | *minimum* | *maximum* | *average* | *number* |
|---|---|---|---|---|
| male | 450 c.M.$^3$ | 655 c.M.$^3$ | 550 c.M.$^3$ | 27 |
| female | 390 c.M.$^3$ | 595 c.M.$^3$ | 478 c.M.$^3$ | 12 |

KEITH estimates in his mentioned article on the skull of the Australopithecus the average for the Gorilla skull as 470 c.M.$^3$ with a maximum capacity of 620 c.M.$^3$. From the very accurate researches of HAGEDOORN it follows, that this amount is too little, because it is already surpassed by that of the female skulls. The general average will have to be taken as easily 500 c.M.$^3$. The found maximum — 655 c.M.$^3$ — also is higher than that mentioned by KEITH [2]) i.e. 620 c.M.$^3$. The dolichocephalic skull had a capacity which agreed with the average for male skulls i.e. 550 c.M.$^3$.

In conclusion mention is still made of the following pecularity of our skull. The determination of the sex in the common type of skull is quite easy, at least when it concerns adult individuals. The mighty developed and strongly projecting canines, together with the often enormous cristae on the skull, are always a true indication of the masculine skull. As regards the sex of our skull I, however, am undecided. The strongly developed canines will lead to think of a masculine skull, but a crista sagittalis is totally absent, the lineae temporales do not even reach the median line. From this we may conclude, to a mediocre development of the musculi temporales; the musculi pterygoidei, on the contrary, appear to have been developed more strongly than in the common Gorilla. DUCKWORTH already remarked[3]) that in the Gorilla as a rule the lamina externa of the Pterygoid is weakly developed, and the Fossa pterygoidea is shallow. In the dolichocephalic Gorilla, this lamina is broad, and the Fossa deep, just as in man. This lesser development of the musculi temporales and stronger development of the musculi pterygoidei may perhaps stand in connection with a somewhat varied mecanism of the so much narrower mandible of the dolichocephalic type.

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[1]) A. HAGEDOORN. Schedelcapaciteit van Anthropomorphen. Ned. Tijdschr. v. Geneeskunde. Jaargang 1923.

[2]) See also A. KEITH. The Growth of Brain in Men and Monkeys. Journ. of Anat. and Phys. Vol. XXIX. 1895.

[3]) W. L. H. DUCKWORTH. Variations in crania of Gorilla savagei. Journ. of Anat. a. Phys. Vol. XXIX. 1895.

**Mathematics.** — *"Ueber projectieve Differentialinvarianten"* III. Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of January 31, 1925).

In dieser Mitteilung zeige ich, wie man aus den, in der ersten Mitteilung abgeleiteten "Klammerausdrücken" invariante Differential*formen* gewinnt. Ferners beweise ich einen Satz über das identische Verschwinden von Klammerausdrücken.

## § 1.

Wenn wir in

$$J = \{K_1, K_2, \ldots, K_{m+2}\} =$$

$$= \begin{vmatrix} q_1 K_1 \ldots q_{m-1} K_{m-1} & q_m K_m & q_{m+1} K_{m+1} & q_{m+2} K_{m+2} \\ p_1 K_1 \ldots p_{m-1} K_{m-1} & p_m K_m & p_{m+1} K_{m+1} & p_{m+2} K_{m+2} \\ \frac{\partial K_1}{\partial t_1} \ldots \frac{\partial K_{m-1}}{\partial t_1} & \frac{\partial K_m}{\partial t_1} & \frac{\partial K_{m+1}}{\partial t_1} & \frac{\partial K_{m+2}}{\partial t_1} \\ \ldots & \ldots & \ldots & \ldots \\ \frac{\partial K_1}{\partial t_m} \ldots \frac{\partial K_{m-1}}{\partial t_m} & \frac{\partial K_m}{\partial t_m} & \frac{\partial K_{m+1}}{\partial t_m} & \frac{\partial K_{m+2}}{\partial t_m} \end{vmatrix} \quad \ldots \quad (1)$$

voraussetzen, dass $K_1, K_2, \ldots, K_{m-1}$ absolute Invarianten sind, dann is

$$q_1 = q_2 = \ldots = q_{m-1} = 0 \quad \text{en} \quad p_1 = p_2 = \ldots = p_{m-1} = 0.$$

Fassen wir dann in (1) die drei letzten Kolonnen zusammen, so gibt die Entwicklung nach LAPLACE:

$$J = \sum_i \begin{vmatrix} q_m K_m & q_{m+1} K_{m+1} & q_{m+2} K_{m+2} \\ p_m K_m & p_{m+1} K_{m+1} & p_{m+2} K_{m+2} \\ \frac{\partial K_m}{\partial t_i} & \frac{\partial K_{m+1}}{\partial t_i} & \frac{\partial K_{m+2}}{\partial t_i} \end{vmatrix} \cdot \frac{\partial (K_1, K_2, \ldots, K_{m-1})}{\partial (t_1, \ldots, t_{i-1}, t_{i+1}, \ldots, t_m)} \quad . \quad (2)$$

Hier ist der zweite Faktor $D^i$ gleich der Funktionaldeterminante von $K_1, K_2, \ldots, K_{m-1}$ bezgl. der Veränderlichen $t_1, t_2, \ldots, t_{i-1}, t_{i+1}, \ldots, t_m$. Gegenüber den Parametertransformationen

$$t_i = t_i(\bar{t}_1, \bar{t}_2, \ldots, \bar{t}_m) \quad , \quad dt^i = \frac{\partial t_i}{\partial \bar{t}_\mu} d\bar{t}^\mu \quad . \quad . \quad . \quad . \quad . \quad (3)$$

sind diese Funktionaldeterminanten kogredient mit $dt^i$. Denn: ist $L_m$ eine $m$-te absolute Invariante, so haben wir:

$$\bar{D} = \frac{\partial (\bar{K}_1, \bar{K}_2, \ldots, \bar{K}_{m-1}, \bar{L}_m)}{\partial (\bar{t}_1, \bar{t}_2, \ldots, \bar{t}_m)} = \Delta \,.\, \frac{\partial (K_1, K_2, \ldots, K_{m-1}, L_m)}{\partial (t_1, t_2, \ldots, t_m)} = \Delta \,.\, D$$

und wegen

$$D = \sum_i \frac{\partial (K_1, K_2, \ldots, K_{m-1})}{\partial (t_1, t_2, \ldots, t_{i-1}, t_{i+1}, \ldots, t_m)} \cdot \frac{\partial L_m}{\partial t_i} = \Sigma\, D^i \cdot \frac{\partial L_m}{\partial t_i}$$

ist also:

$$\overline{D} = \sum_\nu \overline{D}^\nu \frac{\partial \overline{L}_m}{\partial \overline{t}_\nu} = \sum_\nu \overline{D}^\nu \cdot \frac{\partial L}{\partial t_i} \frac{\partial t_i}{\partial t_\nu}$$

$$D^i = \frac{1}{\Delta} \cdot \overline{D}^\nu \frac{\partial t_i}{\partial \overline{t}_\nu} \qquad \ldots\ldots\ldots \qquad (4)$$

Wir können also in (2) $D^i$ statt $dt^i$ schreiben. Ersetzen wir dann noch $K_m$, $K_{m+1}$ und $K_{m+2}$ durch $K_1$, $K_2$ und $K_3$, so ergibt sich der *Satz:*

*Sind* $K_1$, $K_2$ *und* $K_3$ *drei Invarianten mit den* $\Delta$*-Gewichten* $q_i$ *und den* $\lambda$*-Gewichten* $p_i$, *dann ist*

$$[K_1, K_2, K_3] = \begin{vmatrix} q_1 K_1 & q_2 K_2 & q_3 K_3 \\ p_1 K_1 & p_2 K_2 & p_3 K_3 \\ dK_1 & dK_2 & dK_3 \end{vmatrix} \qquad \ldots\ldots \qquad (5)$$

*eine projektiev-invariante Differentialform met* $\Delta$*-Gewicht* $q_1+q_2+q_3$ *und mit* $\lambda$*-Gewicht* $p_1+p_2+p_3$.

Wir haben auch:

$$[K_1, K_2, K_3] = \Sigma\, dK_1 (q_2 p_3 - q_3 p_2) \cdot K_2 K_3 = K_1 K_2 K_3 \cdot \Sigma (q_2 p_3 - q_3 p_2) \cdot d(\log K_1)$$

$$\frac{[K_1, K_2, K_3]}{K_1 K_2 K_3} = d \log \left(K_1^{q_2 p_3 - q_3 p_2}\, K_2^{q_3 p_1 - q_1 p_3}\, K_3^{q_1 p_2 - q_2 p_1}\right) \qquad \ldots \qquad (6)$$

Hieraus folgt z.B., dass $[K_1, K_2, K_3] = 0$ die Abhängigkeit

$$K_1^{\alpha_1} K_2^{\alpha_2} K_3^{\alpha_3} = const. \qquad \ldots\ldots\ldots \qquad (7)$$

gibt.

Weiters folgt aus (5) — analog mit den Gleichungen (29), (30) und (31) der ersten Mitteilung — dass die Klammerausdrücke $[K_1, K_2, K_3]$ die folgenden Relationen erfüllen:

$$[K_1, K_2, K_3 + K_4] = [K_1, K_2, K_3] + [K_1, K_2, K_4] \qquad \ldots \qquad (8)$$

$$[K_1, K_2, K_3 K_4] = [K_1, K_2, K_3] \cdot K_4 + [K_1, K_2, K_4] \cdot K_3 \qquad \ldots \qquad (9)$$

$$\left[K_1, K_2, \frac{K_3}{K_4}\right] = [K_1, K_2, K_3 .] K_4^{-1} - [K_1, K_2, K_4] \cdot K_3 K_4^{-2} \qquad . \qquad (10)$$

## § 2.

Nehmen wir jetzt für $K_1$, $K_2$ und $K_3$ die Invarianten

$$U = (u'y) \quad , \quad X = (v'x) = (y y_1 \ldots y_m x)$$

dann ergibt (5) die beiden Invarianten:

$$[U_1, U_2, X] = \begin{vmatrix} 0 & 0 & (v'x) \\ (u_1'y) & (u_2'y) & (m+1)(v'x) \\ (u_1'dy) & (u_2'dy) & (dv'x) \end{vmatrix} = (v'x) \,.\, (\pi'y)\,(\pi'dy) \;,\; (\pi_{ik}' = (u_1' u_2')_{ik})$$

und

$$[U, X_1, X_2] = \begin{vmatrix} 0 & (x_1 v') & (x_2 v') \\ (u'y) & (m+1)(x_1 v') & (m+1)(x_2 v') \\ (u'dy) & (x_1 dv') & (x_2 dv') \end{vmatrix} = -(u'y) \,.\, (\pi v')\,(\pi\, dv') \;, \quad (\pi_{ik} = (x_1 x_2)_{ik}).$$

Wir erhalten so die beiden mit einander dualen Invarianten:

$$Y = (\pi^m\, y\, dy) = m!\,(\pi' y)\,(\pi' dy) = m!\, \Sigma\, \pi_{ik}'\, (y\, dy)_{ik} \quad . \; . \quad (11)$$

und

$$V = (\pi'^m\, v' dv') = m!\,(\pi v')\,(\pi\, dv') = m!\, \Sigma\, \pi_{ik}\, (v' dv')_{ik} \quad . \quad (12)$$

$Y = 0$ gibt die Tangente $\overline{y\, dy}$; $V = 0$ ist die Gleichung des mit der Tangente bezgl. des Asymptotenkegels konjugierten linearen $R_{m-1}$.

$Y$ hat das △-Gewicht 0 und das $\lambda$-Gewicht 2; $V$ hat das △-Gewicht 2 und das $\lambda$-Gewicht $2(m+1)$. Die Ueberschiebung beider gibt Nul wegen

$$(v' dy) = -(y\, dv') = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

Aus $U, X, Y$ und $V$ leiten wir weiters ab:

$$R = [X, Y, V] = 2Y\, [(xv')\,(\pi'^m\, v' d^2 v') - 2\,(x\, dv')\,(\pi'^m\, v' dv')]$$

$$S = [U, Y, V] = 2V\,(u'y)\,(\pi^m\, y\, d^2 y) - 2\,(u'd\, y)\,(\pi^m\, y\, d\, y)];$$

hieraus durch Ueberschiebung:

$$\mathop{\Sigma}_{ik} \frac{\partial R}{\partial \pi_{ik}} \cdot \frac{\partial S}{\partial \pi_{ik}'} = -4m!\, UXYV \,.\, F_2^2,$$

wo

$$F_2 = (v'\, d^2 y) = (y\, d^2 v') = -(dy dv') = (y y_1 \ldots y_m\, y_{ik})\, dt\, dt^k \quad . \quad (14)$$

die erste quadratische Differentialform ist. Dadurch ist $F_2$ und also auch

$$A = |\,(v'\, y_{ik})\,| = |\,(y y_1 \ldots y_m\, y_{ik})\,| \quad . \; . \; . \; . \; . \; . \quad (15)$$

gewonnen. $F_2$ hat das △-Gewicht 1 und das $\lambda$-Gewicht $m+2$.

Wir zeigen nun noch, wie auch die kubische Differentialform auf diese Weise erhalten werden kann. Es ist

$$M = [X, F_2, A] = \begin{vmatrix} (xv') & F_2 & (m+2)\,A \\ (m+1)(xv') & (m+2)\,F_2 & m\,(m+2)\,A \\ (xdv') & dF_2 & dA \end{vmatrix}$$

$$M = (xv')\,[F_2 \,.\, dA + (m+2)\,A \,.\, dF_2] - 2\,(m+2)\,(xdv') \,.\, AF_2 \quad . \quad (16)$$

$M$ hat das $\triangle$-Gewicht $m+4$ und das $\lambda$-Gewicht $m^2+4m+3$. Weiters:

$$N=[U, F_2, A]=\begin{vmatrix} 0 & F_2 & (m+2)\,A \\ (u'y) & (m+2)\,F_2 & m(m+2)\,A \\ (u'dy) & dF_2 & dA \end{vmatrix}$$

$$N=(u'y)\,.\,[(m+2)\,AdF_2-F_2dA]-2\,(m+2)\,(u'dy)\,AF_2. \quad . \quad (17)$$

$N$ had das $\triangle$-Gewicht $m+3$, das $\lambda$-Gewicht $m^2+3m+3$.

Wenn wir nun $[M, N, A]$ berechnen, so finden wir:

$$[M, N, A]=12\,(m+2)^2\,.\,A^2\,F_2{}^2\,.\,F_3. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

wo

$$F_3=(m+2)\,A\,[3\,dF_2-2\,(v'd^3y)]-3F_2\,.\,dA \quad . \quad . \quad . \quad (19)$$

die gesuchte kubische Differentialform. Sie hat das $\triangle$-Gewicht $m+3$ und das $\lambda$-Gewicht $m^2+3m+2$.

Die Invariante

$$C=[U, X, A]=\begin{vmatrix} 0 & (xv') & (m+2)\,A \\ (u'y) & (m+1)\,(xv') & m\,(m+2)\,A \\ (u'dy) & (x\,dv') & dA \end{vmatrix}$$

oder

$$C=C\,(x, u')=(m+2)\,A\,[(u'y)\,(xdv')-(u'dy)\,(xv')]-(u'y)\,(v'x)\,.\,dA \quad (20)$$

ist eine lineare Differentialform und $C\,(x, u')=0$ gibt einen besonderen, mit dem Punkte $y$ invariant verknüpften, linearen Konnex.

## § 3.

Setzen wir in (1) voraus, das

$$J=\{K_1, K_2, \ldots, K_{m+2}\}\equiv 0\,\{y\} \quad \text{und} \quad \not\equiv\,\{K\} \quad . \quad . \quad . \quad (21)$$

d.h. $J$ verschwindet identisch, wenn wir alle $K_i$ durch die $y$, $y_\alpha$, $y_{\alpha\beta}, \ldots$; ausdrücken; $J$ verschwindet dagegen nicht identisch, wenn wir die $K_i$ als unabhängige Veränderliche betrachten.

Zufolge (21) ist $\frac{p_i}{q_i}$ nicht konstant; sei z.B.

$$\frac{p_{m+1}}{q_{m+1}} \neq \frac{p_{m+2}}{q_{m+2}}, \quad \text{also} \quad \delta=p_{m+1}\,q_{m+2}-p_{m+2}\,q_{m+1}\neq 0.$$

Daher sind die Gleichungspaare

$$\left.\begin{aligned} p_{m+1}\,r_i+p_{m+2}\,s_i&=p_i \\ q_{m+1}\,r_i+q_{m+2}\,s_i&=q_i \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

für $i=1, 2, \ldots, m$ auflösbar. Die $m$ Invarianten

$$K_i'=\frac{K_i}{K_{m+1}^{r_i}\,K_{m+2}^{s_i}} \qquad (i=1, 2, \ldots, m)$$

sind dan *absolute* Invarianten und aus

$$\{K_1, K_2, \dots, K_{m+2}\} \equiv 0 \qquad \{y\}$$

folgt (vgl. die letzten Gleichungen der ersten Mitteilung) dass auch

$$J' = \{K_1', K_2', \dots, K_m', K_{m+1}, K_{m+2}\} \equiv 0 \qquad \{y\}$$

ist.

Nun haben wir aber:

$$J' = (-1)^m \cdot \delta \cdot K_{m+1} \cdot K_{m+2} \cdot \frac{\partial(K_1', K_2', \dots, K_m')}{\partial(t_1, t_2, \dots, t_m)};$$

also auch:

$$\frac{\partial(K_1', K_2', \dots, K_m')}{\partial(t_1, t_2, \dots, t_m)} \equiv 0 \qquad \{y\} \quad . \; . \; . \; . \; . \; . \quad (23)$$

Weiters ist

$$\frac{\partial(K_1', \dots, K_m')}{\partial(t_1, \dots, t_m)} = \sum_{(\alpha_1, \dots, \alpha_m)} \frac{\partial(K_1', \dots, K_m')}{\partial(y_{\alpha_1}, \dots, y_{\alpha_m})} \cdot \frac{\partial(y_{\alpha_1}, \dots, y_{\alpha_m})}{\partial(t_1, \dots, t_m)},$$

also wegen (23), für jedes System $\alpha_1, \alpha_2, \dots \alpha_m$:

$$\frac{\partial(K_1', \dots, K_m')}{\partial(y_{\alpha_1}, \dots, y_{\alpha_m})} \equiv 0 \qquad \{y\}.$$

Deshalb existiert wenigstens eine Beziehung

$$\Phi(K_1', K_2', \dots, K_m') \equiv 0 \qquad \{y\}$$

und daher auch wenigstens eine Identität der Gestalt

$$\Psi(K_1, K_2, \dots, K_{m+2}) \equiv 0 \qquad \{y\} \quad . \; . \; . \; . \; . \; . \quad (24)$$

zwischen allen $m + 2$ Invarianten $K_i$, wobei diese als Funktionen der $y, y_\alpha, y_{\alpha\beta}, \dots$ betrachtet werden. (Als Funktionen der $m$ Parameter $t_i$ sind bereits $m + 1$ Invarianten stets untereinander abhängig).

Existiert umgekehrt eine Beziehung (24), die sich als Identität zwischen $m$ absoluten Invarianten schreiben lässt, so kann man aus ihr auf

$$\{K_1, K_2, \dots, K_{m+2}\} \equiv 0 \ \{y\}$$

schliessen.